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The Oxidation of Pulps with Lead Tetraacetate

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THE OXIDATION OF PULPS WITH LEAD TETRAACETATE

A thesis submitted by

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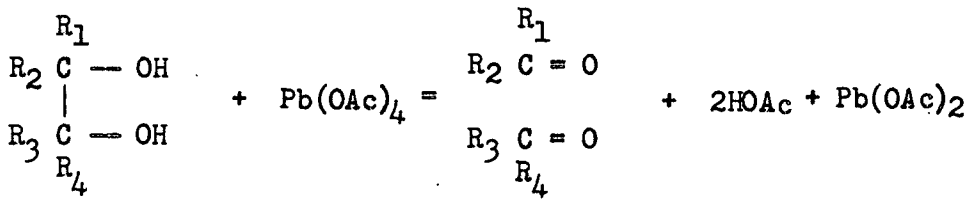
INTRODUCTION AND ANALYSIS OF PROBLEM

In addition to glucose units, an important hexose unit that is found in most cellulose pulps, especially softwoods, is mannose. Now mannose differs from glucose only in the configuration of the 2-carbon atom. Mannose has a cis-glycol configuration of the 2,3-carbon atoms and glucose has a 2,3 trans-glycol configuration.

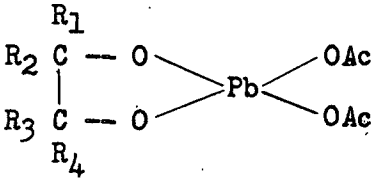
As might be expected, this difference in structure may cause differences in response in the polymers to reactions involving the glycol group. There is evidence, for example, that the nonglucose units (including mannose) in cellulose are among the factors involved in the acetylation behavior of cellulose, influencing both the haze and filtration characteristics (1-4).

The oxidation of the glycol grouping by lead tetraacetate is generally considered to be similar to the more common oxidation with periodic acid (5). The investigation of the tetraacetate oxidation of sugars was initiated by Criegee (6-8) and extended to sugar derivatives by Hockett and collaborators (9-14); both investigators found that lead tetraacetate in a glacial acetic acid solution oxidizes the glycol grouping to pairs of carbonyl groups at rates that are greater for cis- than trans-isomers and are dependent upon the particular glycol examined.

Criegee illustrated the reaction as follows:



Rigby (15) has postulated the presence of the following cyclic intermediate during the reaction:



The intermediate then decomposes to yield the products found by Criegee. The stereochemistry involved in the formation of the intermediate might explain the faster oxidation of cis-glycols. The intermediate illustrates a particular mechanism and may not be the only mechanism.

Dimler (16) has stated that the necessity for both hydroxyls to be engaged in a co-ordination complex before oxidative cleavage can occur would account for the difference in rate of oxidation of cis- and trans-1,2-diols. As the hydroxyls become farther apart in space, co-ordination becomes more difficult and the rate of complex formation and subsequent oxidation decreases.

While in the usual stereochemical formula, written by the Fischer or Hayworth conventions, the hydroxyls are depicted as cis or trans, these formulas do not give a true representation. Actually, the rings are generally not planar, but puckered, which alters the relative position of the hydroxyl groups. (Perhaps, in some cases, the trans-

hydroxyls may be closer together than the cis-hydroxyls.) Dimler's conclusion is that, for simple sugars, the cis configuration is oxidized more readily than the trans, but the configuration of the remainder of the molecule is important in determining the rate of oxidation.

In a more recent series of studies, Perlin and collaborators (17-19) extended the investigation to oligosaccharides, as well as sugars, and also found mannose, a sugar having a 2,3 cis-glycol configuration, to be more easily oxidized than glucose, having a 2,3 trans-glycol configuration. In addition, it was found (19) that in some oligosaccharides, glycol groups which resist oxidation are encountered; such groups are 2,3-trans glycols of central residues which are linked to adjacent residues by 1,4-glycosidic bonds. The 2,3-trans glycols of the reducing and nonreducing ends are readily oxidized and, therefore, as suggested by Perlin, the end-groups are sensitive to oxidation. The author stated (18) that, although the oxidation may involve an initial attack on the α-hydroxyhemiacetal end-group, the configuration of the remainder of the molecule markedly affects the rate of the oxidation.

Steinmann and White (1), in 1954, extended the investigation to the tetraacetate oxidation of bleached wood pulps in a heterogeneous, glacial acetic acid system (prior investigations on sugars had been conducted in a homogeneous medium) and obtained oxidation curves of which the following is typical:

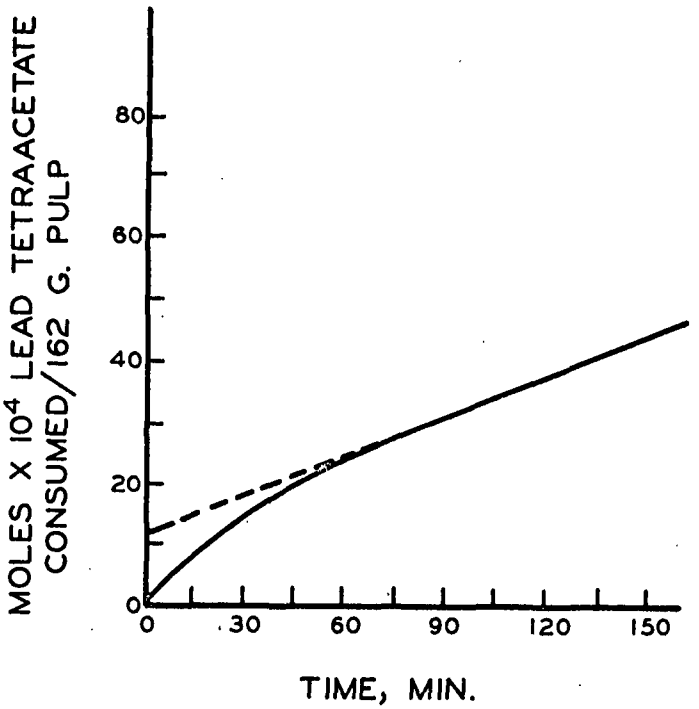


Figure 1. Typical Oxidation Curve Obtained By Steinmann and White (1)

Steinmann and White have extrapolated the linear portion of the curve to the ordinate of the graph and have defined this value of the tetraacetate consumption as the "rapid initial consumption" of oxidant. They concluded, by means of a multiple correlation analysis, that "52% of the variance in lead tetraacetate consumption was due to mannan, only 12% to pentosans, and the remainder (36%) probably due to the reaction with amorphous cellulose." An excellent correlation between the mannose unit content of a pulp and this extrapolated consumption value of lead tetraacetate was obtained and they hypothesized that the cis-glycol grouping of the mannose unit was the basis for the correlation.

Using the investigations of Steinmann and White as a guide, Roudier and Nick (20) attempted to formulate a technique for the determination of mannan in two mannan-containing pulps. They found mannose units to be attacked during the tetraacetate oxidation but only to the extent of 16-40% of the total fraction of mannose units present. They concluded that the oxidation is not suitable for the determination of mannose units. In addition, the authors found during the oxidation of several pulps containing xylose units, that xylose was oxidized (to a lesser extent than mannose) and that the oxidation is, therefore, not specific for mannan. The authors believe that lead tetraacetate penetrates with difficulty into the pulp and, therefore, that accessibility is important.

A subsequent investigation of the oxidation of wood pulps by Matsuzaki and Ward (21), however, indicated that, although a correlation between the mannose unit content and consumption of lead tetraacetate existed for various pulps, the mannose itself was not lost during the reaction to the extent which would be expected were the process one of selective oxidation of mannose units; these investigators stated that no selective oxidation of mannose units took place and hypothesized that variations in the initial consumption of oxidant that occur among different wood pulps during the tetraacetate oxidation might be correlated with the accessibilities of the pulps or with reactions between the oxidant and the end-groups, either reducing or nonreducing. Their hypothesis is supported by data that show an increase in the initial lead tetraacetate consumption of a pulp with increased degree of hydrolysis, despite a decrease in total mannose unit content during hydrolysis.

Prior to the planning of an experimental program, the methods and techniques of Steinmann and White (1) and Matsuzaki and Ward (21) were evaluated.[a] Such an evaluation revealed:

1. Straightforward calculations based upon the previous investigations showed that the quantities of lead tetraacetate consumed in all studies were extremely low; even after a reaction time of two hours, the consumption of tetraacetate was approximately one mole per 500 moles anhydroglucose (one mole of anhydroglucose is taken to equal 162 grams of pulp). Therefore, although a correlation between mannose unit content and tetraacetate consumption was obtained from the oxidation curves, the oxidations probably were too limited in extent to show a selective mannose removal. It was desirable, then, to increase the degree of oxidation.

2. Since lead tetraacetate is a strong oxidant, it may be subject to a loss in strength during an oxidation due to impurities in the glacial acetic acid or to photodecomposition (22). It was not established from the literature whether or not the consumption of oxidant due to the "blank" alone had been thoroughly evaluated. The "blank" consumption must be known in order that the consumption of lead tetraacetate due to the presence of the pulp may be evaluated.

3. The influence of accessibility and number of end-groups of a pulp has been suggested by previous workers; however, no data have been obtained regarding these variables. The experimental program, then, was

[a] The work of Roudier and Nick (20) was not known to this investigator (R.W.D.) until the laboratory work pertaining to this thesis had been completed. However, prior knowledge would not have changed the evaluation.

designed to provide information concerning the importance of accessibility and degree of polymerization (a measure of the number of end-groups).

4. A consideration of the interaction between pulp properties indicated that the experimental program should employ statistics in the analysis of the results. For example, an attempt to evaluate the influence of the degree of polymerization of a pulp by the technique of comparing the oxidation curves of a hydrolyzed and unhydrolyzed sample suffers from the almost certain change of accessibility and hemicellulose content of the sample upon hydrolysis. Similarly, an attempt to evaluate the mannose or xylose content of a pulp by the technique of extracting the sample with alkali suffers from the change in accessibility upon extraction.

The experimental program, then, was designed so that eight pulps could be quite extensively characterized. An oxidation curve was then obtained for each pulp and the important variables evaluated. As anticipated, an interaction between pulp properties was found but a statistical evaluation indicated their relative importance.

5. No mention has been made of the determination of pulp yield after oxidation and no report has been given concerning an investigation of oxidation solutions. The investigation, then, included studies of these "secondary" points.

From a study and evaluation of the literature, an experimental program was designed that would provide fundamental information concerning the factors that influence the oxidation of pulp with lead tetraacetate.

CHARACTERISTICS OF PULPS

PULPS

The International Committee for Cellulose Analysis (ICCA) has selected a series of eight "standard" pulps for evaluating methods of characterizing cellulose. The pulps, numbered 1 through 9 (Pulp No. 6 is no longer obtainable), were obtained from the following distributors:

Samples 1-5 were obtained from Mr. E. E. Hambree, Buckeye Cellulose Corporation, Memphis, Tennessee. Samples 7-9 were obtained from Miss Karin Wilson, Skoghallsverken, Skoghall, Sweden.

Table I lists the data that were available from the distributors regarding these pulps.

ACCESSIBILITIES

DISCUSSION

A physical method—the water-regain, or sorption ratio, method of Howsmon (24)—and a chemical method—the "hydrochloric acid-residue," or hydrolysis method which was developed by Nickerson (25-27) and modified by Philipp and collaborators (28)—were used to determine the accessibilities of the eight pulps.

On theoretical grounds, since the oxidations were made in a non-swelling, acetic acid medium, a "nonswelling method" might have been employed for the determination of accessibilities—one method being the chromium trioxide oxidation technique of Glegg (29).

TABLE I

AVAILABLE DATA—ICCA "STANDARD" PULPS

Pulp No.	Description of Pulp	Cuprietylenediamine Intrinsic Viscosity cm.^{3}/g.[a]	Alkali Resistant Cellulose, % In 10% NaOH[b]	Alkali Resistant Cellulose, % In 18% NaOH[b]	Pentosans, %[c]
1	Cotton Linters	1230	89.9	99.5	0.4
2	Sulfite Pulp, Acetate Grade	910	95.4	97.6	1.1
3	Prehydrolyzed Kraft	550	97.1	98.4	0.9
4	Sulfite Pulp, Soft-wood, Rayon Grade	619	90.4	94.0	2.1
5	Sulfite Pulp, Cello-phane Grade	410	84.3	91.9	1.4
7	Sulfite Pulp, Paper Grade	890	85.7	88.3	4.6
8	Sulfite Pulp, Grease-proof Grade	935	83.6	85.1	5.9
9	Sulfite Pulp, Birch, Rayon Grade	545	88.2	92.5	3.7

[a] C.C.A. Method 28:57 (23)

[b] C.C.A. Method 8:55

[c] C.C.A. Method 24:57

After further consideration, however, it was decided that determinations by the two independent, more rapid methods would be more desirable since (1) the chromium trioxide method is an extremely tedious method, (2) there is some objection (30) to the use of the data of one type of oxidation to indicate the importance of another, and (3) since Mark (31) has stated that all accessibility methods, both chemical and physical, in both swelling and nonswelling media, rank various cellulose fibers in the same order.

SORPTION RATIO

Duplicate samples were dried in weighing bottles at 105°C. for five hours, cooled in a desiccator, and weighed. The samples were then conditioned for 114 hours at 73°F. and 50% relative humidity, and then reweighed. The moisture regain and the sorption ratio (the regain of the sample divided by the regain of Sample No. 1, cotton linters) were then calculated. Table XVI, in the Appendix, lists these data.

Valentine (32) has found that within a relative humidity range of 20-70% and at moderate temperatures, the sorption ratio is independent of temperature. Sorption occurs mainly, if not entirely, in the noncrystalline regions of a polymer (33) and depends upon the hydroxyl groups present in the noncrystalline region.

HYDROLYSIS CRYSTALLINITIES

In this method, samples consisting of 0.2 g. of pulp were hydrolyzed for given durations of time with 50 ml. of 4N hydrochloric

acid at 100°C. and, after correction for the weight of the humic products that formed, the extrapolated percentage residue at zero-time (crystallinity) was found.

In the general equation,

$$\underline{R} = \underline{C} + \underline{A} = \underline{C}_o e^{-\underline{k}_c \underline{t}} + \underline{A}_o e^{-\underline{k}_a \underline{t}},$$

where

$\underline{R}$ = unhydrolyzed portion or residue at time $\underline{t}$ (units of weight);
$\underline{C}$ = crystalline portion at time $\underline{t}$ (units of weight);
$\underline{A}$ = amorphous portion at time $\underline{t}$ (units of weight);
$\underline{C}_o$ = initial crystalline portion (units of weight);
$\underline{A}_o$ = initial amorphous portion (units of weight);
$\underline{k}_c, \underline{k}_a$ = rate constants (units of reciprocal time); and
$\underline{t}$ = time of hydrolysis (units of time).

Since $\underline{C}_o$ is much greater than $\underline{A}_o$, and since $\underline{k}_a$ is much greater than $\underline{k}_c$, after several hours $\underline{A}_o e^{-\underline{k}_a \underline{t}}$ will vanish, and

$$\log \underline{R} = \log \underline{C}_o - \underline{k}_c \underline{t}.$$

A plot of the logarithm of per cent residue *vs.* time may be extrapolated to zero-time in order to obtain the crystallinity. Crystallinity, as determined by this method, is a measure of the lack of accessible 1,4-glycosidic bonds in the sample.

The curves obtained by following this procedure are given in the Appendix (Figures 16a and 16b). All curves are the straight lines determined by the "least-squares" method, and the correlation coefficient for each curve is given. Included in the Appendix are the equation and method employed in applying the "humic acid" corrections to the residue percentages.

In Table II, a comparison is made between the sorption ratios and the percentage crystallinities that were determined for the "standard" pulps.

TABLE II

COMPARISON OF SORPTION RATIOS AND HYDROLYSIS CRYSTALLINITIES

Sample Numbers	Sorption Ratios	Crystal-linities, %
1	1.00	94
2	1.14	94
4	1.18	95
5	1.15	93
9	1.16	95
3	1.32	86
7	1.37	86
8	1.35	86

It is apparent then, from either method, that 5 of the pulps are rather "inaccessible" and 3 of the pulps are "moderately" accessible.

DEGREE OF POLYMERIZATION

The "nitrate viscosity method" was used in this investigation in order to estimate the "weight-average" degree of polymerization (D.P.). The nitrate method is generally considered to be the most suitable for the determination of viscosity from the standpoint of minimum degradation during the reaction and uniformity of the derivative.

It should be noted that the determination of the number of end-groups of cellulose is related to the "number-average" D.P. By means of osmotic measurements the number average D.P. may be estimated (34).

If subsequent investigations were to reveal that the D.P. of a pulp sample was an important influence in governing the extent of the tetra-acetate oxidation of the sample, then a number-average D.P. would be determined by osmotic measurements in order to more thoroughly evaluate this factor.

The cellulose nitrates were prepared by the method of Timell and Bennett (35). The method, which employs a nitrating solution consisting of nitric acid, acetic acid, and acetic anhydride (43:32:25, w/w) has been claimed to yield cellulose nitrates consisting of the theoretical trisubstitution product (14.15% nitrogen). The nitrated pulps were dissolved in ethyl acetate and viscosities were obtained at 25°C. in a Cannon-Fenske No. 50 straight-type viscometer—a viscometer giving small kinetic energy and surface tension corrections (36).

The intrinsic viscosity of each pulp was obtained by an extrapolation to zero concentration, by the Martin technique (37), of a plot of the logarithm of the reduced viscosity *versus* concentration. Figure 15, in the Appendix, gives this plot.

Since the constant K that relates intrinsic viscosity and D.P. varies with the degree of nitration, since the intrinsic viscosity itself varies with the degree of nitration, and since the cellulose nitrates were not completely trisubstituted, it was important that the equivalent intrinsic viscosity of the cellulose trinitrate be determined.

The nitrogen contents of the eight cellulose nitrate samples were determined by the Analytical Department of The Institute of Paper Chemistry by the use of the modified Kjeldahl method of Timell and Purves (38);

from these data, the intrinsic viscosities of the cellulose trinitrates (14.15% nitrogen) were calculated by the use of the Lindsley and Frank equation (39):

$$\log \frac{[\eta]_T}{[\eta]} = \log f_{\underline{x}} + (14.15 - \underline{x})\underline{B}$$

where

$[\eta]_T$ = intrinsic viscosity of cellulose trinitrate;
$[\eta]$ = intrinsic viscosity of cellulose nitrate sample;
$\underline{x}$ = per cent of nitrogen of the cellulose nitrate sample;
$\underline{B}$ = empirical constant = 0.114 for all cellulose samples; and
$f_{\underline{x}}$ = 1.833 - 0.0589 $\underline{x}$ (this function considers the departure of the unit molecular weight from that of the cellulose trinitrate due to the lower degree of nitration).

Table XV, in the Appendix, gives these data.

When the intrinsic viscosities of the cellulose trinitrates were compared with the cupriethylenediamine intrinsic viscosities of the ICCA pulps, some discrepancies were observed. The cupriethylenediamine viscosity, an alkaline viscosity, is influenced greatly by the presence of alkali-sensitive groups, such as carbonyl groups (40). Determinations of the copper numbers (Hagglund modification) (41) of the unoxidized pulps are measures of these reducing groups (see Table III); Pulp Nos. 1 and 8, for example, have about equal nitrate viscosities but quite different cupriethylenediamine intrinsic viscosities. In all probability, the oxidation level of Pulp No. 8 is greater than Pulp No. 1 (since the copper number of Pulp No. 8 is greater than Pulp No. 1). Thus, a portion of the discrepancies between alkaline and nitrate viscosities may be explained by means of the copper number. Pulp Nos. 7 and 2, and 9 and 3 are other examples.

TABLE III

COMPARISON OF TRINITRATE AND CUPRIETHYLENEDIAMINE VISCOSITIES

Pulp No.	Trinitrate Intrinsic Viscosity, dl./g.	Hagglund Copper Number	Cupriethylenediamine Intrinsic Viscosity, $cm.^3/g.$
1	29.9	0.2	1230
8	29.1	1.5	935
7	22.9	0.6	890
2	19.7	0.2	910
4	15.0	1.0	619
9	14.3	1.1	545
3	14.2	0.2	550
5	10.3	1.0	410

Once the appropriate constant K has been obtained by an independent measurement of the molecular weight, the D.P. of a sample may be calculated from the intrinsic viscosity of the trinitrate from the relationship: $D.P.^{\alpha} = K \times [\eta]_T$.

Newman, Loeb, and Conrad (42), by means of sedimentation velocity-diffusion measurements, have determined K for cellulose nitrate dissolved in ethyl acetate at 25°C. to be 80 (% nitrogen = 13.60%). Following the procedure of Timell (35), this value was converted, by means of the Lindsley and Frank equation, to a K corresponding to the trinitrate whereby the relationship became: $D.P. = 67.2 \times [\eta]_T$.

Flory and co-workers (43), by means of light-scattering measurements, obtained the relationship: $[\eta] = 2.50 \times 10^{-5} \bar{M}_w^{1.01}$, using a cellulose nitrate containing 13.5% nitrogen. Again, when the constant was converted to a value corresponding to the trinitrate, and the molecular weight was converted to D.P. ($\bar{M}_w = 297 \times D.P.$), the equation became: $D.P.^{1.01} = 103.26 [\eta]_T$.

Finally, included in the C.C.A. cupriethylenediamine method is the suggested D.P. conversion (23): the equation $D.P.^{0.905} = 0.75[\eta]$ is based upon the work of Immergut, Schurz, and Mark (44) who have determined the constant through osmotic measurements.

Table IV compares the D.P.'s that have been determined by these methods.

TABLE IV

COMPARISON OF VARIOUS DEGREES OF POLYMERIZATION

Pulp No.	Trinitrate Viscosity, dl./g.	"Nitrate D.P." Flory's Constant[a]	"Nitrate D.P." Newman's Constant[b]	Cupriethylenediamine D.P. C.C.A. Method[c]	Cupriethylenediamine Viscosity, $cm.^3/g.$
1	29.9	2851	2009	1889	1230
2	19.7	1885	1324	1354	910
3	14.2	1364	954	774	550
4	15.0	1440	1008	885	619
5	10.3	993	692	561	410
7	22.9	2190	1539	1321	890
8	29.1	2775	1956	1395	935
9	14.3	1374	961	768	545

[a] $D.P.^{1.01} = 103.26 \times [\eta]_T$ (43)

[b] $D.P. = 67.2 \times [\eta]_T$ (35,42)

[c] $D.P.^{0.905} = 0.75\,[\eta]$ (23,44)

where $[\eta]_T$ = trinitrate intrinsic viscosity

It is apparent from the table that the D.P.'s that have been obtained using Newman's constant agree more closely with the cupriethylenediamine D.P.'s; this does not imply that Newman's conversion is more accurate than Flory's, however. It does indicate that the present methods that are available for the determination of the conversion constant K are not in agreement.

Viscosities, then, were used throughout this investigation in the correlations that were made.

SUGAR UNITS CONTENT

A sugar unit may be defined as an anhydrohexose unit with a unit molecular weight of 162 or an anhydropentose unit with a unit molecular weight of 132 (in contrast with the molecular weight of a hexose or pentose: 180 and 150, respectively).

The pulps were hydrolyzed by the method of Saeman and co-workers (45). Saeman has incorporated, into his hydrolysis procedure, correction factors to account for the loss of sugars during the hydrolysis. Therefore, the sugar unit weights that were determined were divided by the following factors to give "corrected weights":

Glucose:	0.974
Mannose:	0.962
Xylose:	0.912

The hydrolyzed pulps were neutralized to pH 3.8 with the carbonate form of IR-45 anion-exchange resin. This neutralization procedure has been found to cause less epimerization than does neutralization with barium carbonate (46). This has been confirmed in the laboratory; an examination of Saeman's procedure using glucose showed no epimerization.

The neutralized hydrolyzates were analyzed quantitatively by a modified chromatographic, spectrophotometric method, developed by Timell, Glaudemans, and Currie (47) and modified by Piper and Bernardin (48), using o-aminobiphenyl as the spray and eluting reagent and obtaining optical densities by means of a Beckman DR quartz spectrophotometer.

This method is given in detail in the Appendix. Included also is a description of the purification procedure of the o-aminobiphenyl. Table XXI, in the Appendix, lists the micrograms of each sugar found for each sample.

Instead of basing the sugar unit percentages on the unoxidized pulp (by the addition of a known amount of D-ribose to the neutralized hydrolyzate prior to spotting), the percentages were calculated on the basis of the total determined sugars since:

1. The ribose moves rapidly on the chromatogram causing large spots and difficulty in obtaining precise results; and
2. Only three sugar spots were visible on the developed chromatograms--glucose, mannose, and xylose.

A comparison of the xylose percentages (determined by two independent methods) given in Table V indicates the agreement for xylose. The precision of the quantitative method may be estimated statistically by determinations using "known" or "standard" sugar solutions. The "coefficients of variation" (49) that were obtained with standard sugar solutions were:

Glucose: 1.48%
Mannose: 2.09%
Xylose: 1.99%

The data and statistical calculations that were needed in order to obtain the above percentages are given in the Appendix II.

SUMMARY OF PULP CHARACTERISTICS

In Table V, the more important characteristics of the eight ICCA "standard" pulps are summarized.

TABLE V

ANALYSIS OF ICCA PULPS

Pulp No.	Description	Residue in 18% $NaOH$, %[a,b]	Total Determined Sugars: Glucose, %	Mannose, %	Xylose, %	Xylan C.C.A. Method 24:57 %[b]	Intrinsic Viscosity: Trinitrate, dl./g.	Cuprietheylene diamine, $cm.^3/g.$[b]	Accessibility: Copper No.	Sorption Ratio	HCl Cryst., %
1	Cotton Linters	99.5	99.5	0.0	0.5	0.4	29.9	1230	0.2	1.00	94
2	Sulfite Pulp, Acetate Grade	97.6	98.5	0.4	1.1	1.1	19.7	910	0.2	1.14	94
3	Prehydrolyzed Kraft	98.4	97.9	1.0	1.1	0.9	14.2	550	0.2	1.32	86
4	Sulfite Softwood Pulp, Rayon Grade	94.0	95.3	2.5	2.2	2.1	15.0	619	1.0	1.18	95
5	Sulfite Pulp, Cellophane Grade	91.9	96.1	2.5	1.4	1.4	10.3	410	1.0	1.15	93
7	Sulfite Pulp, Paper Grade	88.3	87.9	7.5	4.6	4.6	22.9	890	0.6	1.37	86
8	Sulfite Pulp, Greaseproof Grade	85.1	83.5	11.4	5.1	5.9	29.1	935	1.5	1.35	86
9	Sulfite Pulp, Birch, Rayon Grade	92.5	95.1	1.1	3.8	3.7	14.3	545	1.1	1.16	95

[a] Alkali-resistant cellulose, per cent insoluble in 18% $NaOH$, C.C.A. method 8:55.

[b] Data available from distributors of pulps.

OXIDATIONS OF PULPS

PROCEDURE

Approximately 0.27 g. of pulp (dried 4 hours in a 105°C. oven) was transferred to a 500-ml. flask and placed in a 50°C. water bath of polyester composition. Stirring was accomplished by means of a magnetic stirrer.

After the pulp was stirred for two hours in 50 ml. of glacial acetic acid (in order to increase the accessibility of the pulp), 110 ml. of a preheated lead tetraacetate solution in acetic acid was transferred to the flask. After a previously selected time of stirring a 25-ml. aliquot was removed from the flask, 55 ml. of a "stopping solution" (10 g. potassium iodide and 50 g. sodium acetate in 100 ml. water) was added, and the iodine which was liberated was titrated with .02N sodium thiosulfate using Thyodene as the indicator. To the pulp and solution remaining in the oxidation flask were added 290 ml. of stopping solution. The oxidized pulp was washed with water, then with ethanol, and stored under ethanol.

By repeating the procedure for different time intervals, other values for a "consumption of oxidant *vs.* time" curve were obtained. In addition, similar "oxidations," run with the absence of pulp, yielded the values necessary for the plotting of a "blank-decay" curve.

Included in the Appendix is a detailed description of the method; included also are the typical calculations used to correct for the "blank"

consumption, and to convert milliliters of thiosulfate into consumption of lead tetraacetate.

The limited extent of the oxidation necessitated the use of a "weight-buret" in order to titrate and determine the small changes in strength of the large amount of lead tetraacetate solution. (The typical calculations given in the Appendix illustrate the need for this precision.)

CHROMATOGRAPHY

During the investigation, the following chromatographic developers and spray reagents were used:

1. Ethyl acetate:acetic acid:water (9:2:2, v/v) (a chromatographic developer). Prior to development, the spotted papers were conditioned overnight in the vapor phase of the solvent;

2. o-Aminobiphenyl (a spray reagent). When used in the quantitative determination of sugars, a 0.4% solution, as described by Timell (47), was prepared (see Appendix II). When used in the qualitative analyses of pulps and oxidation solutions, a 2% solution of the phosphate salt was prepared. The latter spray is Rapson's modification (50) of Timell's preparation (47). The spray reagents are sensitive to reducing sugars;

3. Silver nitrate (a spray reagent). The dried chromatogram is dipped into a 3% silver nitrate solution (in 95% acetone). After air drying, the paper is sprayed with a 2% sodium hydroxide solution (in 95% ethanol). The paper is allowed to dry 5-10 minutes to develop the spots. The chromatogram is then dipped into a concentrated solution of sodium thiosulfate (350 g. per liter), thoroughly washed with water, and allowed to dry in air. The spray is sensitive to most organic compounds. The procedure is essentially that described by Trevelyan (51) and modified by Pearl and Darling (52); and

4. p-Anisidine hydrochloride (a spray reagent). The spray is sensitive to reducing sugars and may be prepared as a 3% solution in n-butanol (53).

DECOMPOSITION OF LEAD TETRAACETATE IN ACETIC ACID

In the dark, at room temperature without agitation, a solution of lead tetraacetate in glacial acetic acid was found to lose oxidizing power slowly; these data are plotted in Fig. 2.

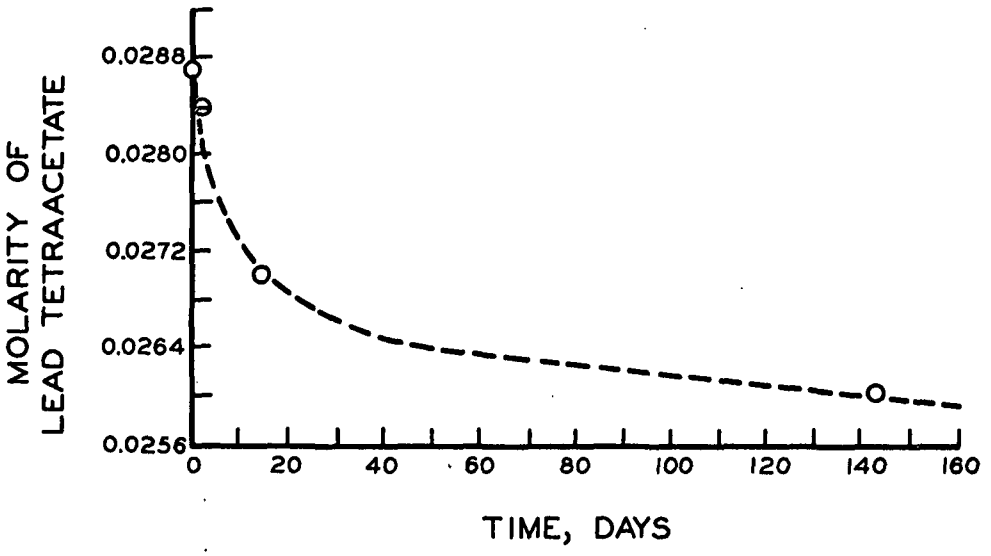


Figure 2. Decrease in Strength of Lead Tetraacetate Upon Standing

As was expected, then, under the conditions of an oxidation (50°C. and moderate agitation) a definite loss in the strength of the lead tetraacetate solution was observed. This change was termed the "blank-decay" loss; during the oxidation of each pulp, a blank-decay curve was obtained in order that the consumption of oxidant due to the pulp alone could be ascertained. Blank-decay curves are given in Figs. 3 and 7 in this section.

THE OXIDATION CURVES

The eight ICCA pulps were oxidized by the procedure described on page 20 (the procedure is given in more detail in Appendix III). In Fig. 3, a representative "blank-decay" curve and an oxidation curve are plotted.

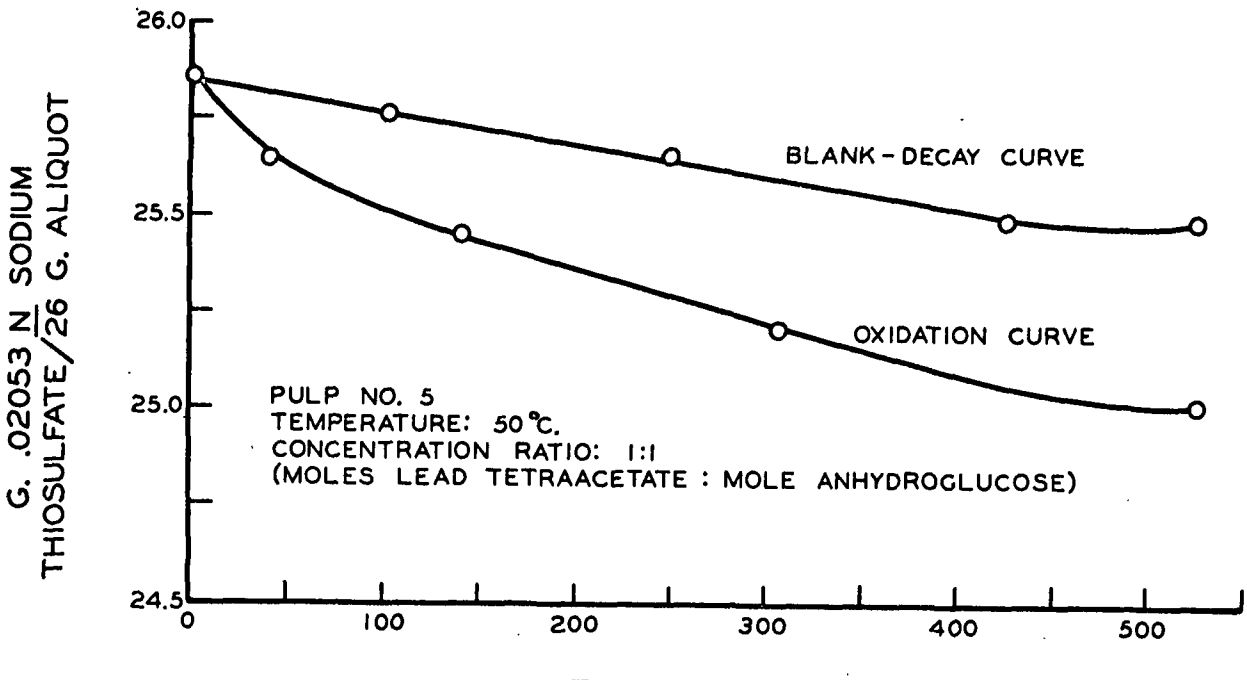


Figure 3. The Oxidation of Pulp No. 5

It will be noticed from Fig. 3, that the values for the ordinate are given in terms of weight rather than volume. In addition, each point on the oxidation curve has been determined independently--that is, from a different sample of the same pulp.

By subtracting the oxidation curve from the "blank-decay" curve, the quantity of thiosulfate consumed by the pulp was ascertained, and

the equivalent amount of lead tetraacetate calculated. These calculations are included in the Appendix.

After approximately eight points had been determined for each pulp by this technique, a series of curves were plotted showing the lead tetraacetate consumption (corrected for the blank) for each pulp. These curves are given in Figs. 4a, 4b, and 4c. Table XXII, in the Appendix, lists the tetraacetate consumption values that were used to plot the curves.

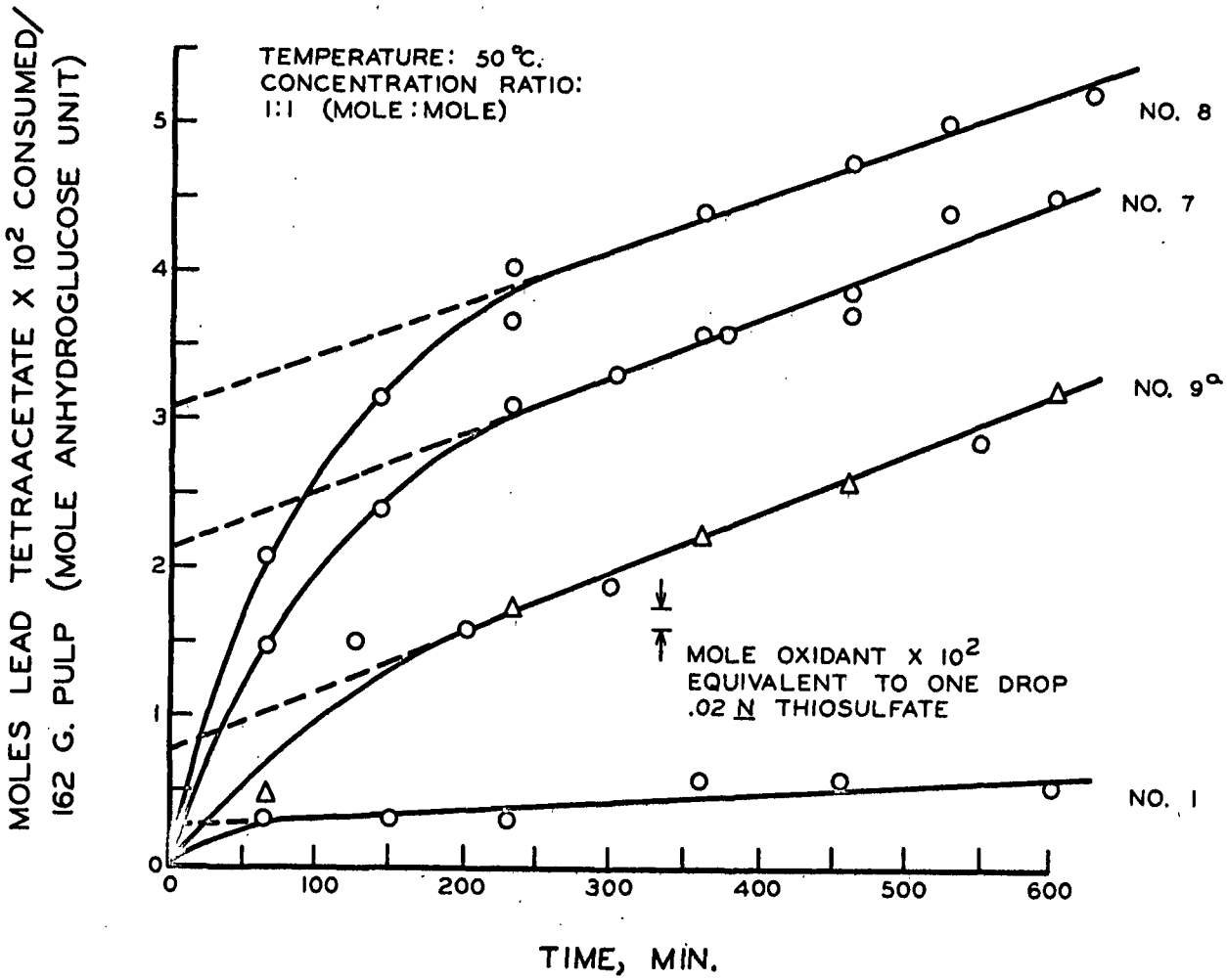


Figure 4a. The Oxidation of the ICCA Pulps

[a] The significance of the triangular and circular points is discussed on pp. 28-30.

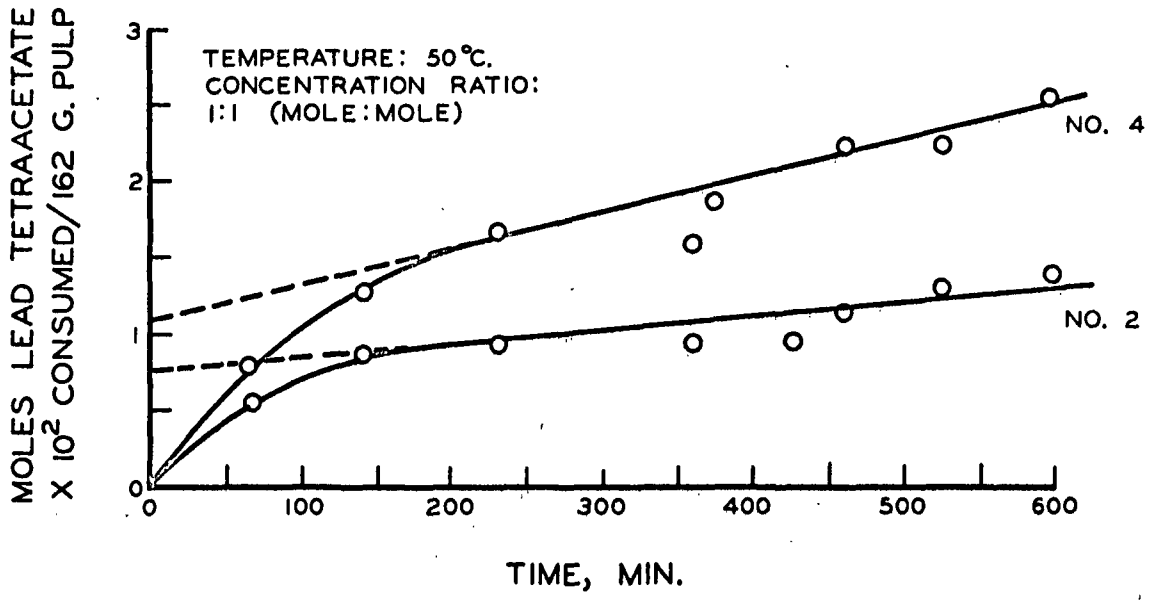


Figure 4b. The Oxidation of the ICCA Pulps

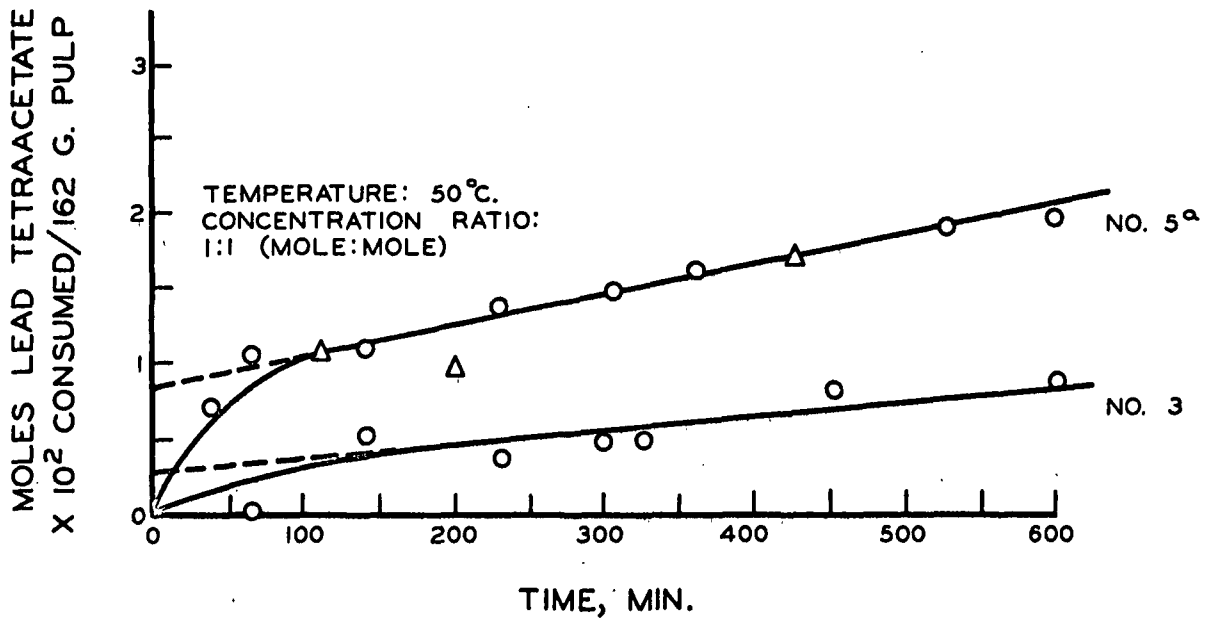


Figure 4c. The Oxidation of the ICCA Pulps

[a] The significance of the triangular and circular points is discussed on pp. 28-30.

THE EFFECTS OF TEMPERATURE AND CONCENTRATION

TEMPERATURE

As expected, the consumption of lead tetraacetate during an oxidation was found to be influenced by the oxidation temperature. Pulp No. 8 was oxidized at 20, 30, and 50°C.; in each oxidation, the concentration of lead tetraacetate [moles lead tetraacetate per mole anhydroglucose unit (162 g. pulp)] was 4:1. Only two points were determined on the "consumption-time" curve during each oxidation since the extent of the oxidation and not the exact shape of the curve was under study.

Figure 5 gives the data that were obtained at 30 and 50°C.:

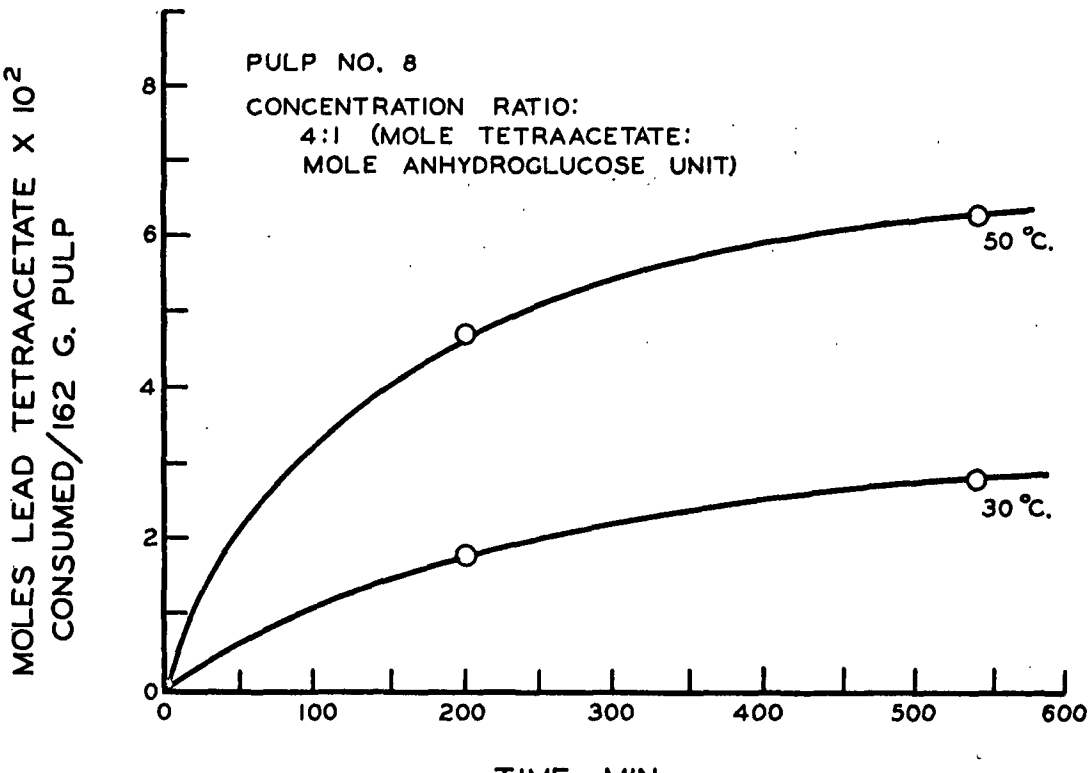


Figure 5. The Effect of Temperature Upon the Oxidation

When the pulp sample was oxidized at 20°C., a white precipitate, presumably a lead salt, formed in the solution.

From the graph, it is seen that temperature has a pronounced influence upon the extent of the oxidation. In order to take advantage of the greater oxidation at 50°C., all pulp samples were oxidized at this temperature.

CONCENTRATION

In order to ascertain the importance of the concentration ratio of lead tetraacetate to pulp (anhydroglucose) during the oxidation, Pulp No. 8 was oxidized at "lead tetraacetate per anhydroglucose unit (162 g. pulp)" ratios of 4:1, 2.5:1, and 1:1 (mole:mole); in each oxidation the temperature was 50°C. In Fig. 6, the results of this investigation are given.

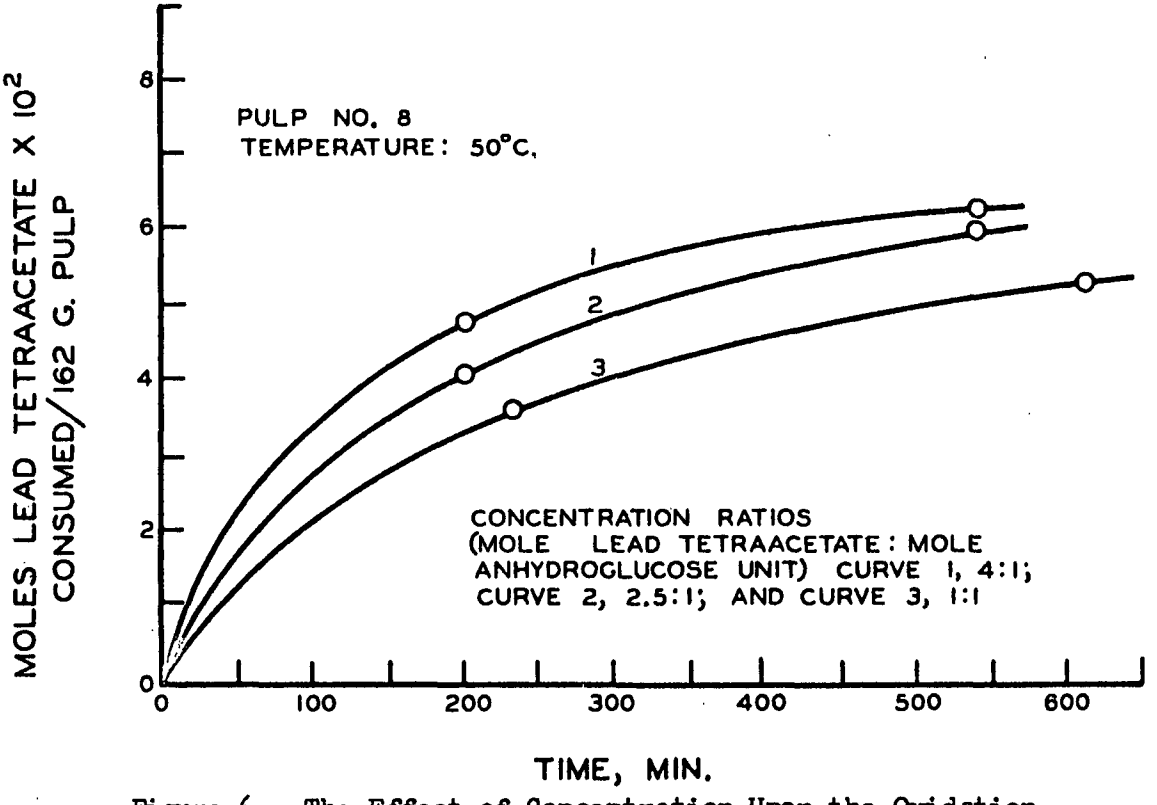


Figure 6. The Effect of Concentration Upon the Oxidation

It may be observed from Figs. 5 and 6, that the "concentration effect" is less pronounced than the "temperature effect."

Since the determination of the lead tetraacetate consumption involves small differences in the back-titration of the oxidant, it is apparent that the lower the initial quantity of lead tetraacetate, the smaller will be the back-titration and, consequently, the more accurate will be the determination of the curve.

It was concluded, then, that an initial lead tetraacetate to pulp ratio of 1:1 (mole:mole) would offer a more reproducible oxidation than a ratio of 4:1 while sacrificing only slightly in the extent of oxidation. On theoretical grounds, this ratio was not reduced below 1:1 since the limiting value of lead tetraacetate consumption should be one mole per mole of anhydroglucose unit (6). [It should be noted that Steinmann and White (1) and Matsuzaki and Ward (21) used a concentration of only 1:4.]

Therefore, the eight pulp samples were oxidized with an initial molar ratio of lead tetraacetate/anhydroglucose unit of 1:1.

REPRODUCIBILITY OF OXIDATIONS

VARIATIONS IN BLANK-DECAY CURVES

For each oxidation a blank-decay curve, of the type given in Fig. 3 was obtained. Although each decay curve was quite similar, variations in the curves were observed--probably as a result of different "lot numbers" of the acetic acid. Figure 7 illustrates this variation.

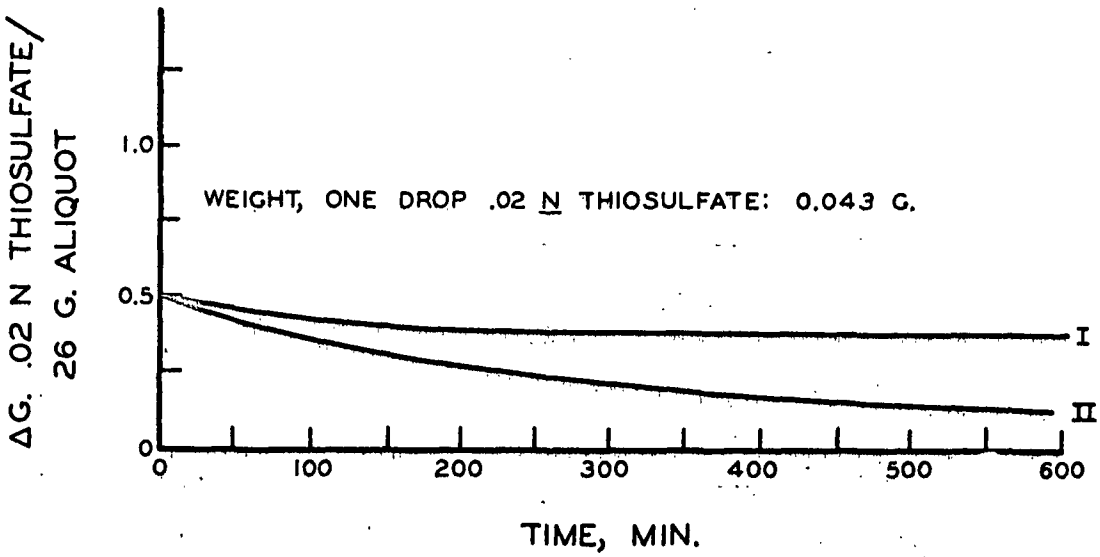


Figure 7. Variation in Blank-Decay Curves

Of approximately 20 blank-decay curves that were obtained during the investigation, 6 curves followed a pattern that is illustrated by the composite curve, Curve I (Fig. 7), while 7 blank-decay curves were nearly identical to the composite curve, Curve II. The variations between Curves I and II initiated the investigation of whether differences in blank-decay curves would cause variations in the resultant "consumption-time" curves for the pulps.

An analysis of the oxidation of Pulp No. 5 (see Fig. 4c) revealed that eight points (indicated by circular points in the figure) were obtained from oxidations in which blank-decay curves similar to Curve II were subtracted; three points (indicated by triangular points in the figure) were obtained from an oxidation in which a blank curve similar to Curve I was subtracted. Ignoring the point that is obviously incorrect, it was concluded that the resultant oxidation curve for a pulp

is independent of the shape of the blank-decay curve (within the moderate range of decay values encountered in these oxidations).

A similar conclusion was obtained by analyzing the data concerning the oxidations of Pulp No. 9. The circular and triangular points (given in Fig. 4a for Pulp No. 9) were obtained from oxidations made on two different days with dissimilar blank-decay curves.

PRECISION OF THE TITRATION

In Table VI, selected data from Fig. 3 are presented:

TABLE VI

ANALYSIS OF CURVES IN FIGURE 3

(Oxidation of Pulp No. 5)

g. .02053N Thiosulfate/26 g. Aliquot	Time of Measurement, min.	Type of Curve
25.85	0	Blank-Decay
25.85	0	Oxidation
25.49	525	Blank-Decay
25.01	525	Oxidation

Through simple calculations, the following figures may be obtained from Table VI:

Basis: 26 g. Aliquot Oxidation Solution

g. .02N thiosulfate consumed during the oxidation (25.85 - 25.01)	0.84
g. .02N thiosulfate consumed by the blank during the oxidation (25.85 - 25.49)	0.36
Therefore, g. .02N thiosulfate consumed by the pulp only	0.48

Therefore, 0.48 g. of .02N thiosulfate represents the oxidant consumed by the sample; furthermore, if eight points are to be determined in order to define the "consumption-time" curve, the difference between points could be represented by 0.06 g. of .02N thiosulfate (.48/8)—one and one-half drops.

Obviously, the second place after the decimal point is significant, and if a smooth, accurate curve is to be determined, these small differences must be measured very carefully. Experimentation with burets, microburets, and weight-burets showed that the use of the latter would provide the needed accuracy. In addition, the use of a weight-buret removes personal "bias" from the collection of data (since only approximate five-milliliter intervals are marked on the buret).

The amount of lead tetraacetate that is equivalent to a full drop of .02N sodium thiosulfate is indicated in Fig. 4a. By the careful manipulation of a weight-buret, a half-drop quantity may be dispensed.

REPRODUCIBILITY OF OXIDATION CURVES

Of primary importance if the oxidations are to be successfully analyzed is the reproducibility of the curves that are obtained for the various pulps.

Since the points in Figs. 4a, 4b, and 4c have been obtained independently of each other, it appears that the curves have been obtained with a rather high precision. Generally, the only appreciable scatter of points is found in the early stages of the oxidation. Two possible reasons for this scatter would be:

1. The lead tetraacetate solution that was added to the pulp at the beginning of the oxidation was not quite at the same temperature as the water bath; hence, the scatter is the result of a small temperature effect.

2. In the early stages of the oxidation, the dependent variable is changing rapidly with respect to the independent variable. Therefore, a small error in the measurement of time could produce a rather large error in the value of lead consumption.

Since each point on each curve in Figs. 4a, 4b, and 4c has been obtained from a different specimen of the pulp sample, there is a possibility that a part of the scatter is due to nonuniform samples. The scatter in the data points is not large enough to alter the analysis of the oxidation, nor the conclusions that will be presented.

FACTORS THAT INFLUENCE THE OXIDATION

ANALYSIS OF OXIDATION CURVES

By an arbitrary extrapolation the linear portions of the oxidation curves to the ordinate (as illustrated in Figs. 4a, 4b, and 4c) a measure of the rapid, initial portion of the lead tetraacetate consumption may be obtained. In Table VII, these extrapolated consumption values of lead tetraacetate are given.

Values other than the extrapolated values of the tetraacetate consumption were obtained by taking values from the curves at other selected times of oxidation. Table XXIII (see Appendix IV) lists some of these

TABLE VII

CONSUMPTION OF LEAD TETRAACETATE (EXTRAPOLATED TO ZERO TIME)

Pulp No.	Moles Lead Tetraacetate x 10^2 Consumed Per 162 g. Pulp (Extrapolated Value)
1	0.26
2	0.76
3	0.27
4	1.08
5	0.85
7	2.14
8	3.07
9	0.76

values. The choice of the extrapolated value is the only one easily explained on theoretical grounds; this will be explained in another section of this report (see DISCUSSION).

ACCESSIBILITY

Using the extrapolated values of the tetraacetate consumption as the dependent variable, a plot of consumption versus sorption ratio was made. Figure 8 gives this correlation.

The straight line plotted in Fig. 8 is the statistical "line-of-best-fit." The correlation coefficient (r) equals 0.67; however, the correlation fails the analysis of variance "F" test [(54), pp. 147-77]. In other words, at the 95% confidence level the correlation coefficient is not significantly different from zero, linear regression cannot be assumed, and no straight line should be drawn.

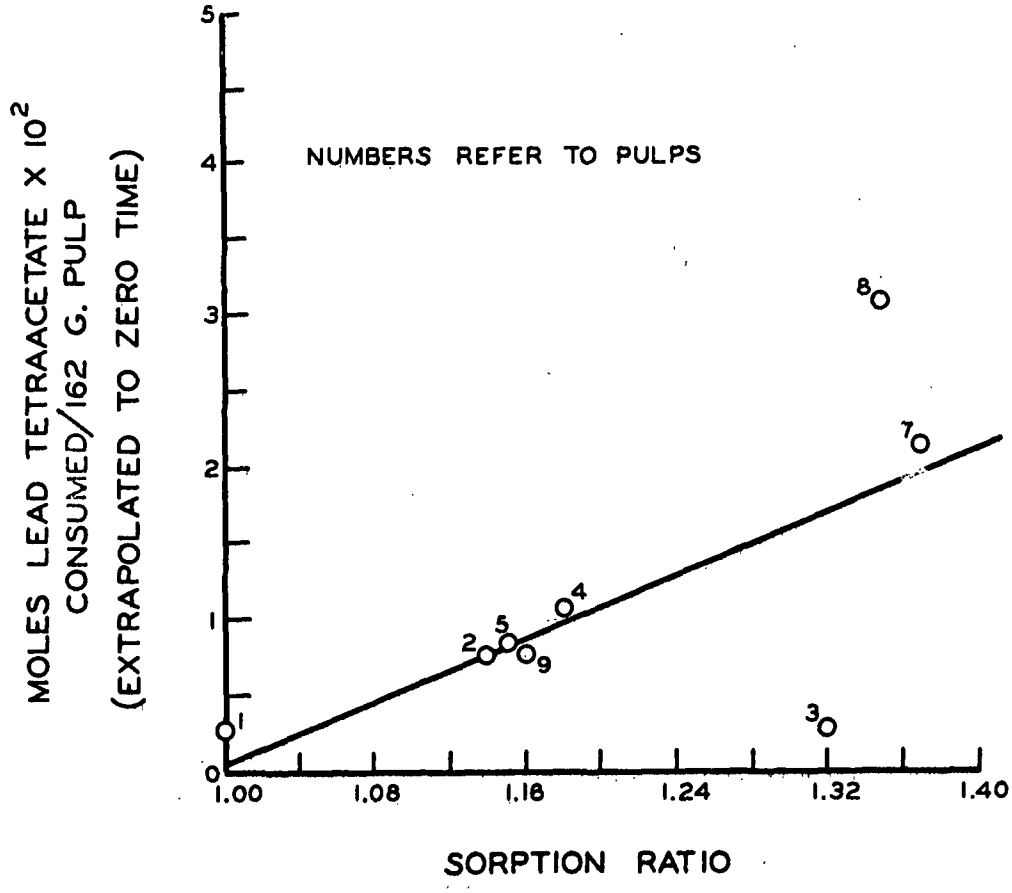


Figure 8. Influence of Sorption Ratio Upon Tetraacetate Consumption

DEGREE OF POLYMERIZATION (AS MEASURED BY THE TRINITRATE VISCOSITY)

In Fig. 9, lead tetraacetate consumption (extrapolated values) is plotted versus the trinitrate intrinsic viscosity in order to ascertain the influence of the end-groups of the pulps.

The correlation coefficient for the straight line is 0.45 and the test for linear regression is negative; thus, at the 95% confidence level, a straight line should not be drawn.

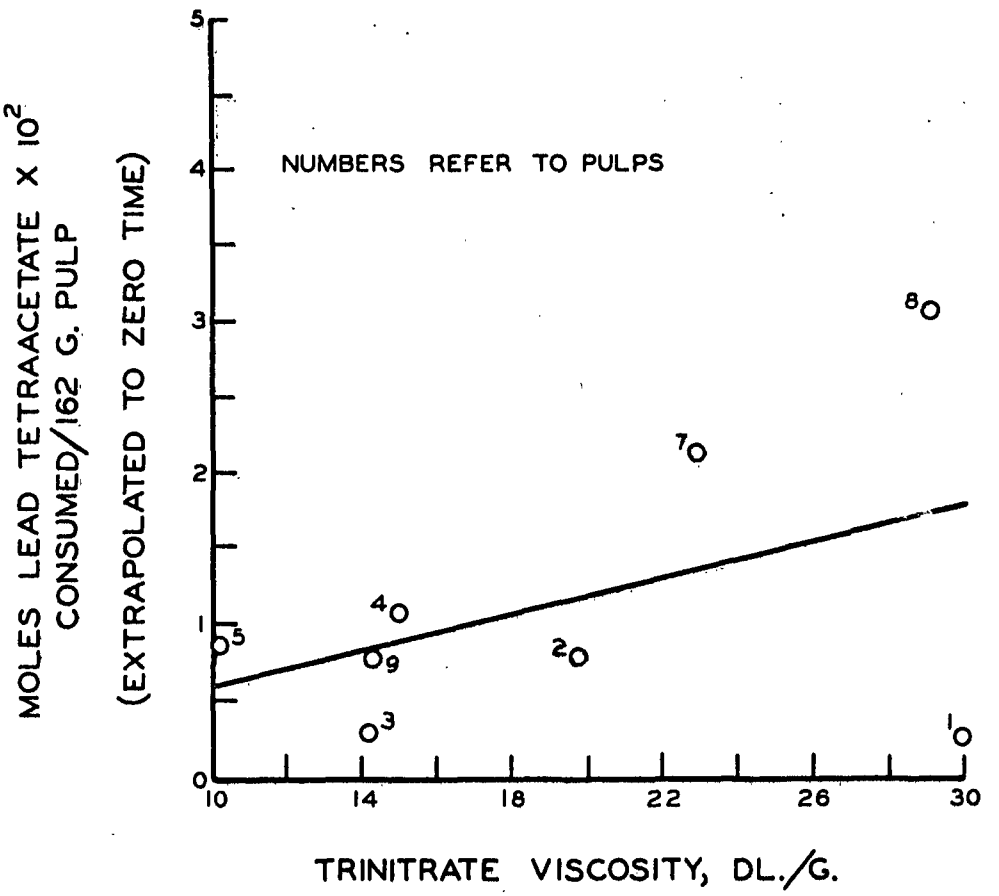


Figure 9. Influence of Trinitrate Intrinsic Viscosity Upon Tetraacetate Consumption

SUGAR UNITS CONTENT

In Figs. 10, 11, 12, and 13, the extrapolated values of the lead tetraacetate consumption are plotted versus various "sugar unit percentage" data. In Figs. 10 and 11, the abscissas are per cent mannose and xylose units, respectively. In Fig. 12 the consumption is plotted versus the sum of per cent mannose and xylose units. In Fig. 13, the abscissa is alkali-resistant cellulose (per cent insoluble in 18% sodium hydroxide).

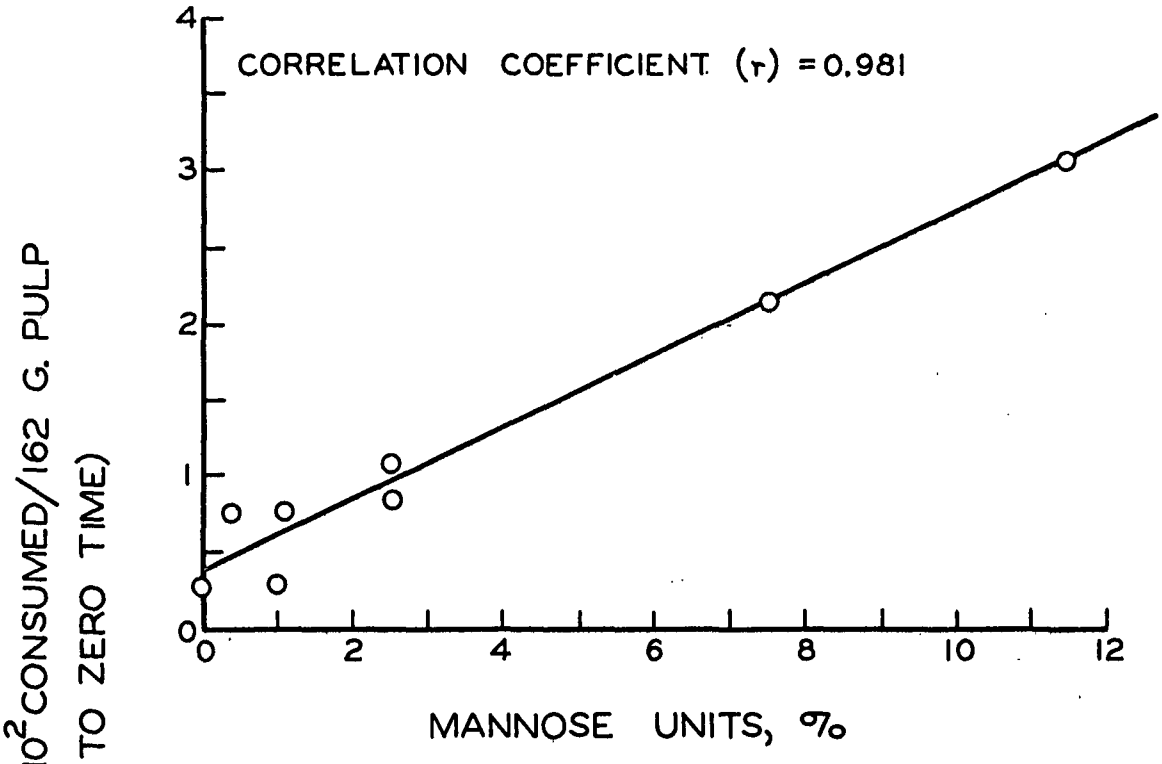


Figure 10. Influence of Mannose Unit Percentage Upon Tetraacetate Consumption

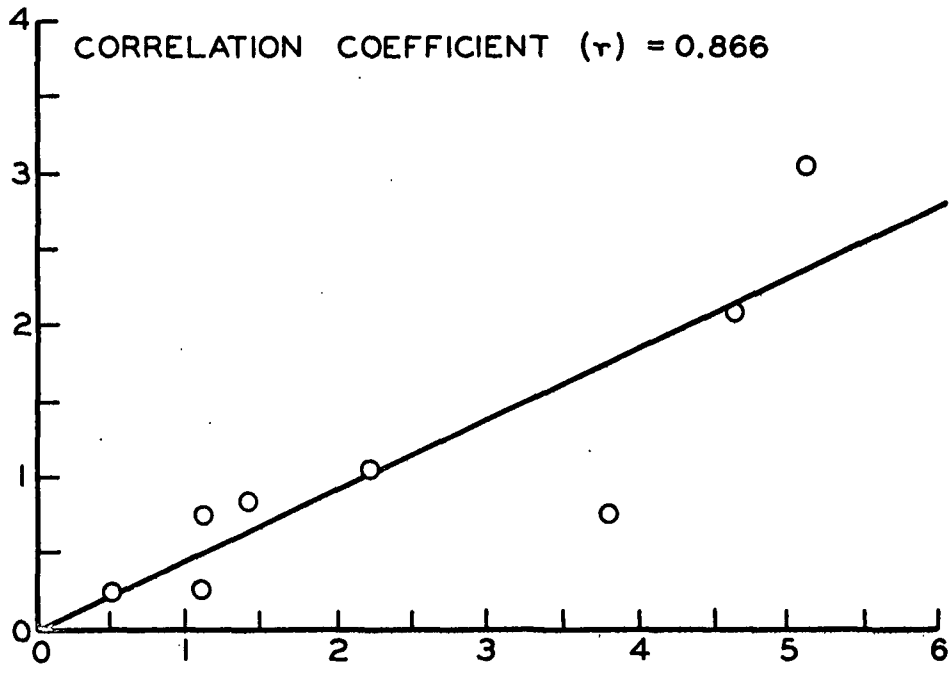


Figure 11. Influence of Xylose Unit Percentage Upon Tetraacetate Consumption

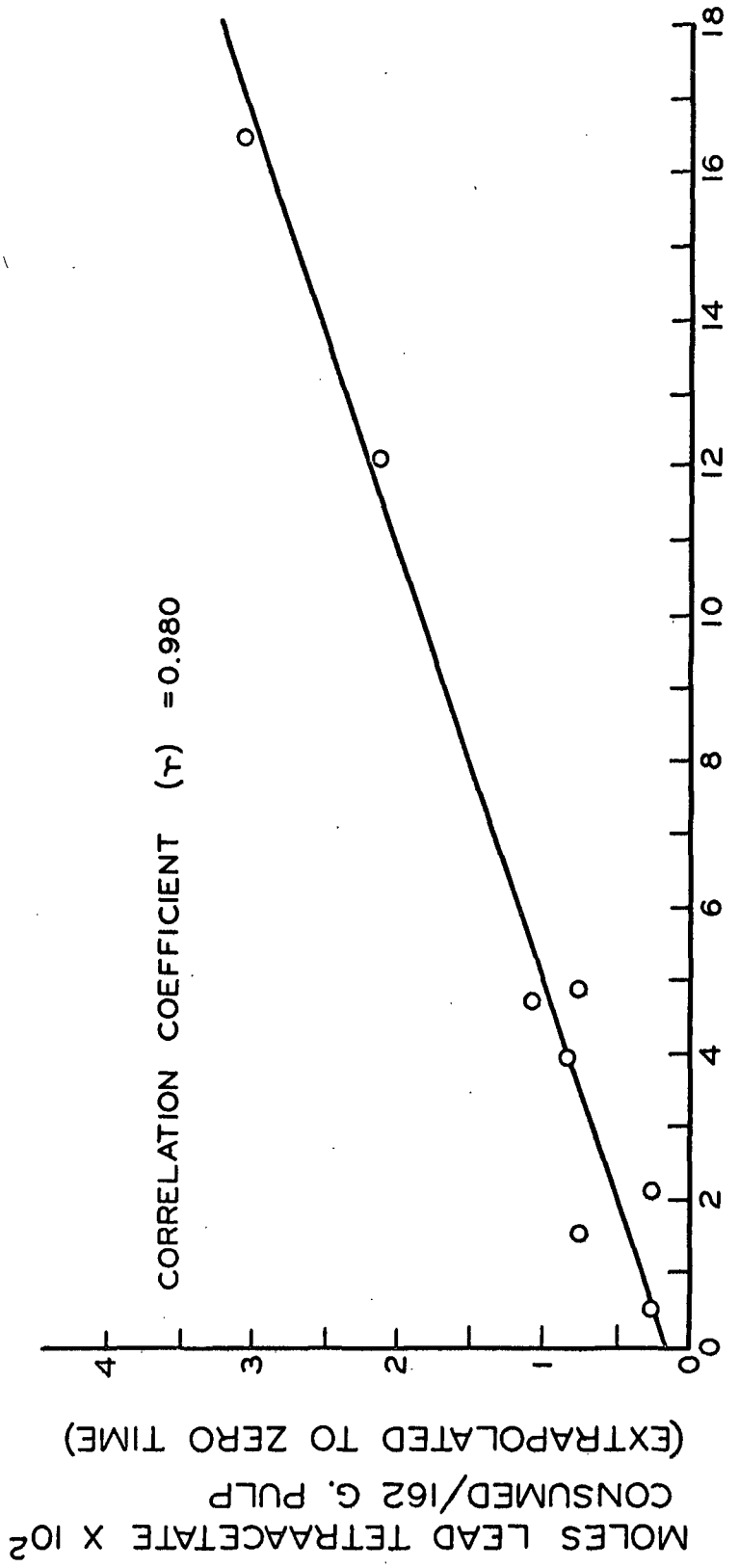


Figure 12. Influence of Mannose + Xylose Unit Percentage Upon Tetraacetate Consumption

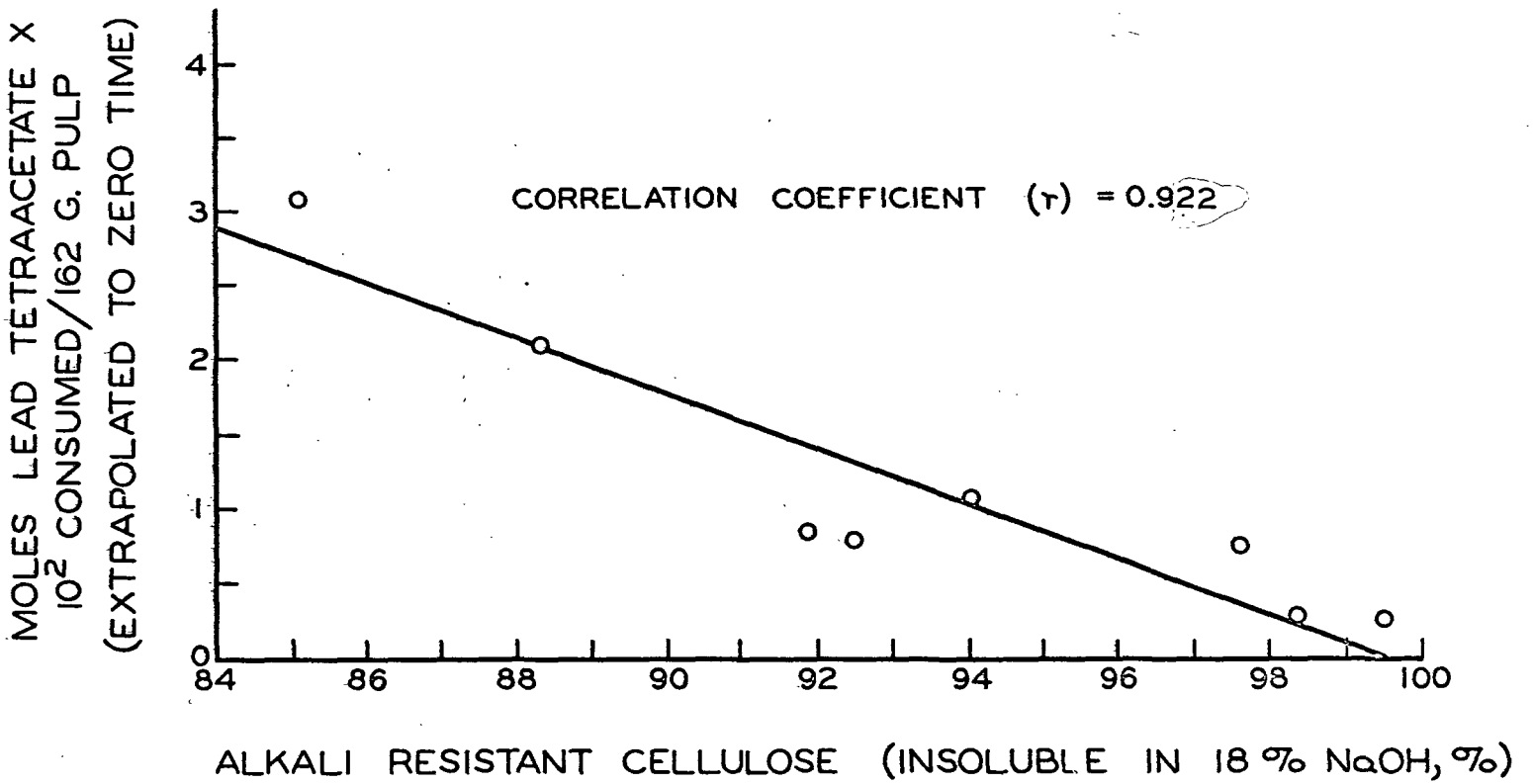


Figure 13. Correlation Between Lead Tetraacetate Consumption and Alkali-Resistant Cellulose

If values of tetraacetate consumption other than the extrapolated values are used for the ordinate, the correlation coefficients that are given in Figs. 10-13 would be altered. Table XXIV, in the Appendix, gives the correlation coefficients that would be obtained for other selected consumption values.

From Figs. 10-13, it can be seen that certain sugar unit percentages of a pulp correlate more closely with the consumption extrapolated to zero time than either the sorption ratio (a measure of accessibility) or the trinitrate viscosity (which gives some correlation with end-groups). More specifically, the mannose unit content of a pulp seems to be more important than the xylose unit content in influencing the extent of the extrapolated portion of the oxidation.

The correlations, then, verify the findings of Steinmann and White (1) and Roudier and Nick (20) who found that, presumably due to the cis-glycol configuration, the mannose unit percentage of a pulp was the most important single factor in the oxidation.

When the xylose unit percentage of a pulp is plotted against the lead tetraacetate consumption after 600 minutes of oxidation, however, an excellent correlation is obtained. This plot is given in Fig. 14. (The values for the ordinate were obtained from Table XXIII, in the Appendix.)

As seen from Fig. 14, the influence of xylose units, while probably not as important as mannose units, is definitely not negligible. Thus, the conclusion of Roudier and Nick (20) is verified. This factor will be discussed further in another section of this report (see DISCUSSION).

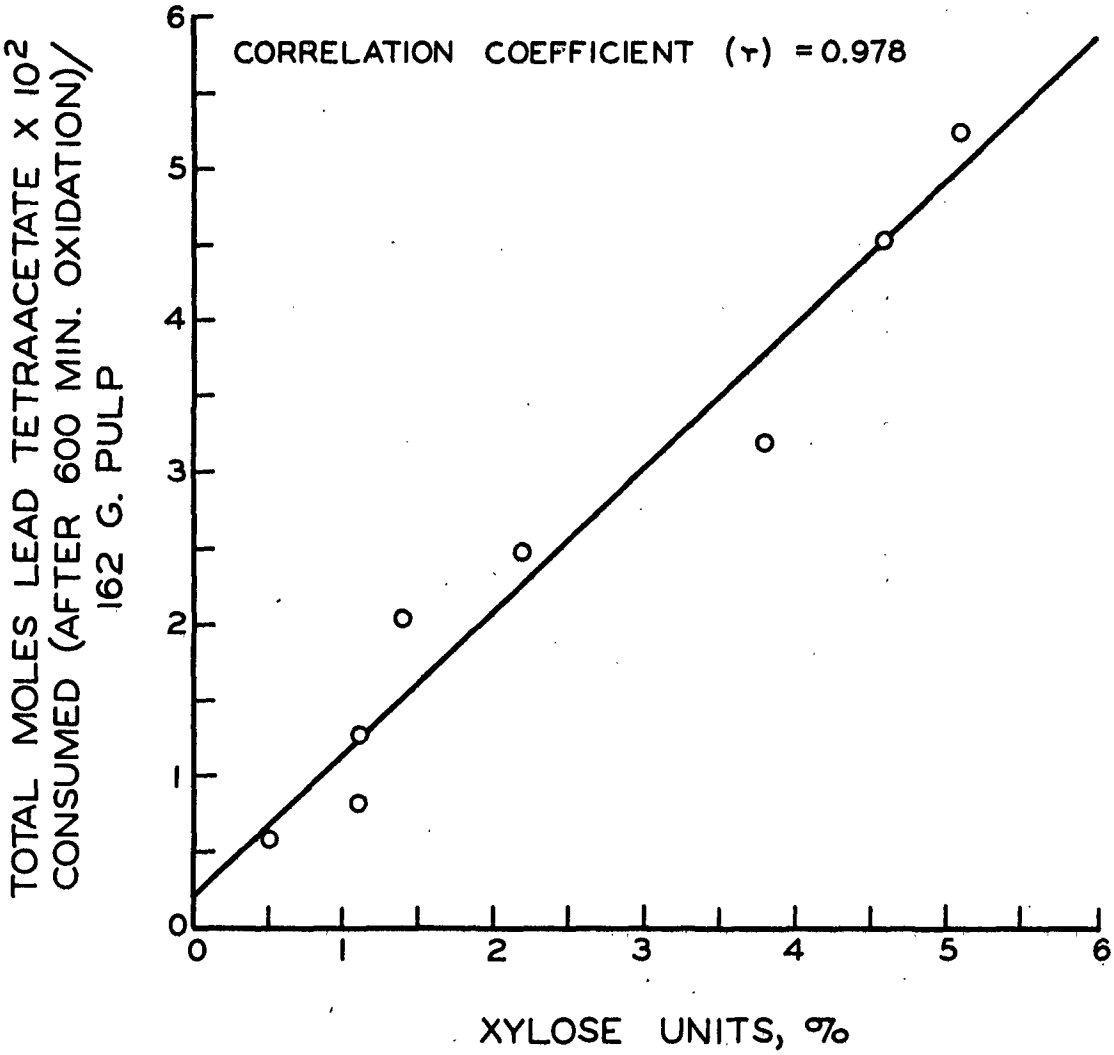


Figure 14. Influence of Xylose Unit Percentage Upon Total Tetraacetate Consumption[a]

[a] Total consumption = consumption after 600 minutes of oxidation.

CORRELATIONS INVOLVING SULFITE PULPS

It should be noted from Fig. 8 (consumption of lead tetraacetate versus sorption ratio), that if the point representing Pulp No. 3 were eliminated, and a revised straight line were drawn, the correlation coefficient would be 0.92 and the "F" test for linear regression would be positive. Pulp No. 3, the prehydrolyzed kraft pulp, was the only kraft pulp under investigation.

If the point representing Pulp No. 1 in Fig. 9 (consumption of lead tetraacetate versus trinitrate viscosity) were eliminated, and a revised straight line were plotted, the correlation coefficient would be 0.88 and the test for linear regression would be positive. It should be noted that the slopes of both the original and the revised lines are contrary to that which would be expected from a review of the work of Matsuzaki and Ward (21) and Perlin and co-workers (17-19); i.e., the higher the viscosity (the fewer the number of end-groups), the greater the oxidation.

Thus, the relationships in both Figs. 8 and 9 are sensitive to one "scattered" point.

If both Pulp No. 1 (cotton linters) and Pulp No. 3 (prehydrolyzed kraft) were neglected, correlations valid for sulfite pulps only could be made in the same manner that has been illustrated in Figs. 8-13. In Table VIII, the correlation coefficients that were computed from this type of analysis are given.

TABLE VIII

SULFITE PULP CORRELATIONS

Abscissa[a]	Correlation Coefficient[b]
Percentage Mannose Units	0.992
Percentage Xylose Units	0.805
Percentage Mannose + Xylose Units	0.980
Alkali-Resistant Cellulose (Per cent Insoluble in 18% NaOH)	0.893
Trinitrate Intrinsic Vis.	0.886
Sorption Ratio	0.929

[a] The ordinates are the extrapolated lead tetraacetate consumption values (Table VII).

[b] Correlations based upon Pulp Nos. 2, 4, 5, 7, 8, and 9 only.

From Table VIII, again it is noticed that a very high correlation between the mannose unit percentage of a pulp and its consumption of oxidant is obtained. It also appears that the accessibilities of the sulfite pulps (as measured by the sorption ratio) influence the oxidations somewhat. [It should be noted that a limited number of pulps were used in obtaining the correlations (6 pulps).]

ANALYSIS OF OXIDIZED PULPS

YIELD

In Table IX, the yields of the eight oxidized pulps are listed as are the respective oxidation times. At the conclusion of each oxidation, a potassium iodide-sodium acetate "stopping solution" was added to the oxidation flask, the pulps were filtered, washed with water, then with ethanol, and stored under absolute ethanol. In order

TABLE IX

YIELDS OF OXIDIZED PULP SAMPLES

Sample No.	Time of Oxidation, min.	Yield, %	Time of Oxidation, min.	Yield, %
1	65	85.9	360	83.0
	150	87.4	455	86.3
	230	84.0	600	87.5
2	65	78.6	425	81.3
	140	83.9	460	83.8
	230	86.2	525	81.5
	360	86.3	600	83.0
3	65	89.4	300	86.5
	65	83.7	255	84.5
	140	82.4	450	85.5
	230	87.9	600	88.8
4	65	91.5	375	84.0
	140	89.7	460	86.6
	230	86.6	525	80.6
	360	82.9	600	85.7
5	40	70.2	305	78.1
	65	81.5	360	75.3
	140	76.6	525	75.5
	230	75.9	600	77.1
7	65	92.2	375	88.8
	140	88.5	460	89.4
	230	88.8	460	89.6
	300	89.4	525	86.9
	360	89.2	600	86.5
8	65	89.1	360	84.7
	140	89.4	460	88.4
	230	89.3	525	90.6
	230	86.6	625	85.5
9	65	91.4	360	90.3
	125	92.5	460	90.6
	200	92.5	550	89.9
	230	90.4	600	89.9
	300	90.7	—	—

to determine yield, the ethanol was removed by filtration, and the oxidized pulp was dried for five hours at 50°C. in vacuum.

It may be noticed from Table IX that there is no correlation between percentage yield and time of oxidation.

Although the mean percentage yield values for the eight oxidized pulps varied over a wide range, a statistical analysis showed that, at the 95% confidence level, there was no significant difference between many of the yield figures. In Table X, using the "t" test for significance (54, p. 384), the mean percentage yield for each pulp is compared in order to ascertain whether significant differences exist.

TABLE X

TEST OF SIGNIFICANT DIFFERENCES BETWEEN MEAN PERCENTAGE YIELD VALUES

(95% Confidence level)[a]

Pulp No.	Mean Yield, %[b]	Pulps Showing Differences Between Mean Yield Values	Pulps Showing No Differences Between Mean Yield Values
1	85.7	5,7,9	2,3,4,8
2	83.1	3,5,7,8,9	1,4
3	86.1	2,5,7,9	1,4,8
4	86.0	5,7,9	1,2,3,8
5	76.3	1,2,3,4,7,8,9	—
7	88.9	1,2,3,4,5,9	8
8	88.0	2,5,9	1,3,4,7
9	90.9	1,2,3,4,5,7,8	—

[a] "t" test for significance (54, p. 384).
[b] Means obtained from values in Table IX.

For example, from Table X, the yield values for Pulp No. 3 are not significantly different from Pulp Nos. 1, 4, and 8, and, therefore, no

comparison, on the basis of yield, may be made between them; the values for Pulp No. 3 are different from the values of Pulp Nos. 2, 5, 7, and 9, however.

It can be seen that the lack of significant differences among the percentage yield values makes any analysis difficult, if not impossible. Only Pulp No. 5, which has a very low yield, and Pulp No. 9, which has a high average percentage yield, are different from every other pulp.

Since a correlation between yield and any other characteristic must involve several pulps to be valid, no correlations were attempted.

In Table XI, the yields of Pulp No. 8, under selected conditions of oxidation and washing are given.

TABLE XI

YIELD OF OXIDIZED PULP NO. 8

Description of Technique	Yield, %
Mean yield, %, from Table IX.	88.0
Yield, %, after 600 minutes "control oxidation" in acetic acid (no lead tetraacetate present).	95.8
Yield, %, oxidized 600 minutes with lead tetraacetate, dried from acetic acid (no water present); occluded acetic acid removed from dried oxidized pulp with ethanol and water to constant weight.	94.3

It should be noted, in Tables IX and XI, that all yield determinations were made by filtration through a Buchner funnel and include mechanical losses.

The significance of Table XI will be discussed in another section (see DISCUSSION). Also, in that section, possible reasons for the "scatter" in the yield data will be advanced.

SUGAR UNITS CONTENTS

The sugar units contents of selected oxidized pulps were determined by the same technique that was employed in the analyses of the unoxidized pulps (see pages 17-18). Table XXI, in the Appendix, lists the micrograms of each sugar found in the determinations.

Tables XIIa and XIIb give the percentages by weight, and total determined sugars, that were found at various times of oxidation.

TABLE XIIa

SUGAR UNITS COMPOSITION OF SELECTED PULPS

Pulp No.	Sugar	Percentage by Weight, Total Determined Sugars[a] Unoxidized, %	After 600 Minutes Oxidation, %
4	Glucose	95.3	97.2
	Mannose	2.5	1.0
	Xylose	2.2	1.8
5	Glucose	96.1	98.0
	Mannose	2.5	0.9
	Xylose	1.4	1.1
9	Glucose	95.1	96.6
	Mannose	1.1	0.4
	Xylose	3.8	3.0

[a] Adjusted to 100%

TABLE XIIb

SUGAR UNITS COMPOSITION OF SELECTED PULPS

Pulp No.	Sugar	Percentage by Weight, Total Determined Sugars[a] Unoxidized, %	After 65 Min. Oxidation, %	After 230 Min. Oxid., %	After 600 or 625 Min. Oxid., %
7	Glucose	87.9	—	94.0	92.0[b]
	Mannose	7.5	—	3.0	4.6
	Xylose	4.6	—	3.0	3.4
8	Glucose	83.5	88.9	89.2	90.6[c]
	Mannose	11.4	7.3	6.6	5.2
	Xylose	5.1	3.8	4.2	4.2

[a] Adjusted to 100%

[b] Samples oxidized 600 minutes

[c] Samples oxidized 625 minutes

Using the mean yield percentage figures of the oxidized pulps (as listed in Table X), the percentages of glucose, mannose, and xylose units, that were lost during the oxidation process may be calculated. (Sample calculations are given in the Appendix.) These data are given in Table XIII. Also given are the grams of sugar units removed per 100 grams of unoxidized pulp.

TABLE XIII

SUGAR UNITS REMOVAL AFTER 600 MINUTES OXIDATION[a]

Pulp No.	Percentages Unoxidized Sugar Units Removed, Glucose, %	Mannose, %	Xylose, %	Grams Sugar Units Removed Per 100 Grams Unoxidized Pulp, Glucose, g.	Mannose, g.	Xylose, g.
4	12.4	64.0	27.3	11.8	1.6	0.6
5	22.2	72.0	42.8	21.3	1.8	0.6
7	6.9	45.4	34.8	6.1	3.4	1.6
8	4.6	59.6	27.5	3.8	6.8	1.4
9	7.7	63.6	29.0	7.3	0.7	1.1

[a] Pulp No. 8 oxidized 625 minutes

Due to the variance of the yield data for a pulp, calculations similar to those employed in the preparation of Table XIII will show the creation of mannose units for Pulp No. 7 between 230 and 600 minutes of oxidation; the same phenomenon is observed for Pulp No. 8 between 230 and 625 minutes of oxidation. This is impossible, of course, and is probably due to scatter in the yield percentage figures.

The calculations, when carried further, using Pulp No. 8 as an example, showed that approximately one-third of the total moles of pulp (anhydroglucose units) lost during the process equaled moles of lead tetraacetate consumed; i.e., one-third of the pulp loss could be attributed to "oxidative removal." The remainder is lost through other nonoxidative processes. A possible explanation of this loss is given in another section of this report (see DISCUSSION).

By comparing the grams of glucose and mannose units present in the unoxidized pulp per gram of xylose unit, with the grams of glucose and mannose units lost per gram of xylose unit lost, Table XIV may be prepared. (Notice, the first group in Table XIV gives the ratios of sugar units originally present in the unoxidized pulps, while the second group gives the ratios of the actual sugar units removed.)

From Table XIV, it can be seen that the mannose unit removal is greater and the glucose unit removal is less than would be the case were the sugar units removed in the same ratio as that in which they exist in the unoxidized pulp.

The significance of Table XIV will be discussed in more detail in another section of this dissertation (see DISCUSSION).

TABLE XIV

COMPARISON OF RATIO OF SUGAR UNITS REMOVED TO ORIGINAL RATIO

Pulp No.	Grams Sugar Units in Unoxidized Pulp Per One Gram Xylose Unit,			Grams Sugar Units Lost Per One Gram Xylose Unit Lost,		
	Glucose, g.	Mannose, g.	Xylose, g.	Glucose, g.	Mannose, g.	Xylose, g.
4	43.3	1.1	1.0	19.7	2.7	1.0
5	68.6	1.8	1.0	35.5	3.0	1.0
7	19.1	1.6	1.0	3.8	2.1	1.0
8	16.4	2.2	1.0	2.7	4.9	1.0
9	25.0	0.3	1.0	6.6	0.6	1.0

IDENTIFICATION OF ERYTHROSE

A cellulosic material that is oxidized with lead tetraacetate or periodate should contain, in part, a structure consisting of erythrose and glyoxal units (55).

If a glucose or mannose unit of a pulp is oxidized by lead tetraacetate, hydrolysis of the oxidized pulp should yield erythrose among its products.

By the method given by Perlin and Brice (56), di-O-formyl-D-erythrose was prepared from glucose and purified by extraction with ethyl acetate. The product was hydrolyzed with hydrochloric acid, neutralized, and concentrated to give D-erythrose. The erythrose concentrate was chromatographed, after preconditioning, using a developer of ethyl acetate:acetic acid:water (9:2:2, v/v) and sprayed with p-anisidine hydrochloride. The chromatograms showed a rather pure preparation, somewhat contaminated with glucose, and giving a large spot having an R_g of 3.3[a].

[a] The R_g number is the ratio of the distance of the spot from the origin and the distance of a glucose spot from the origin.

A composite one-gram sample of Pulp No. 8 (consisting of residual samples of pulp oxidized various durations of time) was subjected to a limited hydrolysis by boiling with 3% sulfuric acid for 5-10 minutes. The acid was removed by filtration and the sample boiled again with "fresh" acid.

After four such "extractions," the combined filtrates were neutralized to pH 5.5 with barium hydroxide. The barium sulfate was removed by a centrifuge and filtration; the neutralized filtrate was then concentrated.

Chromatography of the concentrated hydrolyzate using ethyl acetate: acetic acid:water (9:2:2, v/v) as the developer and o-aminobiphenyl and silver nitrate as the sprays showed a spot that, it was concluded, was erythrose since (1) the spot had traveled the same distance from the origin as the adjacent erythrose "known," and (2) the spot was visible after spraying with o-aminobiphenyl--a spray sensitive to reducing sugars. It is believed that this is the first time that erythrose has been identified in a hydrolyzate from a tetraacetate-oxidized pulp.

It may be concluded then, that a mechanism of the lead tetraacetate oxidation of polysaccharides is similar to that of simple sugars; i.e., the 2,3-glycol grouping is cleaved to form the dialdehyde.

ANALYSIS OF OXIDATION SOLUTION

In order to investigate the oxidation solution, at the conclusion of a selected oxidation, a small quantity of water (equal in volume to the water in the "stopping solution") was added to the oxidation mixture.

The mixture was filtered and, by means of an IR-120 cation-exchange column, lead ions were removed from the filtrate. The column was washed until a negative Molisch test was obtained.

The lead-free solution, plus the column-washings, were concentrated and analyzed chromatographically. Using ethyl acetate:acetic acid:water (9:2:2, v/v) as the developer and both o-aminobiphenyl and silver nitrate as the spray reagents, the chromatograms were found to yield streaks from the origin through the glucose spot (plus a light mannose spot).

Since the o-aminobiphenyl spray reagent is sensitive to reducing sugars, presumably the streaking is caused by the presence of soluble partly oxidized oligosaccharide fragments in the oxidation solution.

The indication of these fragments in the oxidation solution would help explain the lowered yields that have been obtained in the oxidized pulps (see Tables IX and XI). The implications of this analysis will be discussed more fully in another section of this report (see DISCUSSION).

DISCUSSION

PROOF OF OXIDATION

That an oxidation of pulp occurs during the reaction between pulp and lead tetraacetate has been assumed frequently in the literature but, it is believed, never proved. There is no reason to assume, however, that an oxidation does not occur. Investigations with simple sugars and sugar derivatives have shown that an oxidation takes place and the consumption of lead tetraacetate during the reaction with pulp is an established fact.

It was noted during the investigation that the pulps, after reaction with lead tetraacetate, were more readily hydrolyzed by Saeman's hydrolysis technique (45) than were the unreacted pulps. One interpretation of this phenomenon is that an oxidation has occurred. In addition, the high correlation between the mannose unit percentages of the pulps and the values of oxidant consumption indicates that an oxidation has occurred.

The fact that the oxidation curves (consumption versus time) have a noticeable "break" after a certain time of reaction is important evidence that an oxidation has taken place. Cramer, Hockett, and Purves (57), while investigating the lead tetraacetate oxidation of cellulose acetate, and Yin and Brown (58), working with the lead tetraacetate oxidation of cellulose nitrate, reported that the break in the curve marked the end of the true glycol oxidation. It was found that cellulose triacetate consumed no oxidant and that no break in the curve was obtained upon the oxidation of cellulose trinitrate.

Most important, of course, is the chromatographic indication of an oxidation product, erythrose, from a hydrolyzate of the oxidized pulp. The presence of this sugar not only indicates that a general oxidation has taken place, but rather that a specific 2,3-glycol oxidation has occurred upon reaction of the pulp with lead tetraacetate.

IMPORTANCE OF CORRELATIONS

During the plotting and analysis of various correlations that were obtained in the investigation, the following "policies" were kept in mind:

1. More importance was placed upon correlations involving the extrapolated consumption values of lead tetraacetate than upon values of consumption obtained at other times during the oxidation. It is believed that the extrapolated values are better measures of the "breaks" in the oxidation curves than are other values. (The importance of the "break" in the oxidation curve has been mentioned in this section.)

More importance was attached, therefore, to the high correlation (0.981) between the mannose unit percentage and the extrapolated tetraacetate consumption (see Fig. 10) than to the high correlation (0.978) between xylose unit percentage and total tetraacetate consumption after 600 minutes of oxidation (see Fig. 14).

2. More importance was placed upon the analysis of the oxidized pulps than upon the correlation coefficients that have been calculated. The number of pulps used in obtaining a correlation coefficient is always

important in a statistical investigation and, when only eight pulps are used, the correlation coefficient is quite sensitive to one "scattered" point.

In Fig. 8 (see page 34) the correlation coefficient between consumption of oxidant and sorption ratio could be increased from 0.67 to 0.92 by the elimination of one point. It is seen, therefore, that it could not be concluded that accessibility (sorption ratio) was unimportant merely from the data of Fig. 8.

FACTORS THAT INFLUENCE THE OXIDATION

1. From Tables XIII and XIV (see pages 47 and 49) it is apparent that mannose units are selectively removed from a pulp during the oxidation (although this removal is not necessarily an oxidative removal); in other words, a greater percentage of mannose units are lost than either glucose or xylose units (see Table XIII). Also, on a gram basis, it is seen from the ratios in Table XIV that the mannose unit removal is greater and the glucose unit removal is less than would be the case were the sugars removed in the same ratio as that in which they exist in the unoxidized pulp.

This selective mannose unit removal thus confirms the conclusion of Roudier and Nick (20). Although the xylose unit removal is not as great as the mannose unit removal, it is appreciable (see Table XIII); also, a small glucose unit removal was found.

Although one cannot doubt the preferential removal of the mannose units as a whole, the question still remains: Is it possible that the

"loss ratio" in Table XIV is actually the ratio of sugar units that exist in the more accessible portion of the pulp so that mannose units are not selectively removed, but rather that all three sugars are "randomly" lost during the process from the accessible fraction of the pulp?

It is believed by this investigator that this is not the case although presumably the accessible fraction of a pulp will be oxidized at a more rapid rate than the crystalline fraction.

It is known that the correlation between the mannose unit percentage and subsequent lead tetraacetate consumption during an oxidation is much greater than the correlation between sorption ratio (accessibility) and tetraacetate consumption. More important, if the aforementioned theory were true, then, as seen in Table XIV, one would be forced to admit that the mannose unit:xylose unit ratio is always higher in the accessible portion than in the "highly ordered" portion of a pulp--a statement never proved. One may conclude, therefore, that mannose units are selectively lost from a pulp under the oxidative conditions employed in this study.

2. Using the yield values of Table XI (see page 45), it is seen that the pulp yield of a "control" in glacial acetic acid (no lead tetraacetate present) is much higher than the mean yield in the oxidative solution (95.8% compared to 88.0%). Furthermore, it can be seen that, under special conditions of washing, the yield of an oxidized pulp is significantly higher than the mean yield of a pulp oxidized under the usual conditions (94.3% compared to 88.0%).

It is hypothesized therefore, that at the conclusion of an oxidation (during the addition of the "stopping solution" and subsequent washing

operations) the glacial acetic acid is diluted to weak acetic acid; the weak acid partially hydrolyzes and/or dissolves the partly oxidized pulp causing oligosaccharide fragments to go into the oxidation solution and, consequently, lower the yield. This theory would help explain (1) the higher yield obtained when the pulp was dried from acetic acid, (2) pulp losses that may be due to nonoxidative processes, and (3) the lack of correlation of yield with time of oxidation.

This theory is substantiated by the indication of partly oxidized oligosaccharide fragments in the oxidation solution (see pages 50 and 51).

3. Since the correlation between the xylose unit percentage and consumption of oxidant is greater when "final consumption values of tetraacetate" are used for the ordinate rather than the initial values (see Fig. 14 and Table XXIV), it is assumed that the oxidation of xylose units is different than the oxidation of mannose units. Xylose, of course, is a trans-glycol, and should oxidize at a slower rate than cis-glycols, and may not be expected to influence the initial portion of the curve.

No doubt there is some relationship between the xylose unit content and the accessibility of a pulp (as between the mannose unit content and accessibility), and, after prolonged oxidation, the oxidation of the accessible regions "masks" the nature of the xylose variable.

Accessibility, as such, may have an effect secondary to the mannose unit content of a pulp in the initial portion of the oxidation.

SUMMARY

From a review of the literature it appeared that the investigation of the following variables would provide information concerning the lead tetraacetate oxidation of wood pulp:

1. The mannose unit content of the pulp;
2. The xylose unit content of the pulp;
3. The accessibility of the pulp; and,
4. The number of end-groups of the pulp.

The pulp samples that were used during the investigation were the eight "standard" ICCA (International Committee for Cellulose Analysis) pulp samples. The pulps were characterized prior to oxidation in the following manner:

1. The sugar units contents of the pulps were determined by a modification of the quantitative (chromatographic), spectrophotometric method of Timell, Glaudemans, and Currie (47).

2. The accessibilities of the pulps were determined by the sorption ratio method of Howsmon (24), a physical method, and by the hydrolysis technique of Philipp and co-workers (28), a chemical method.

3. An estimation of the number of end-groups in the pulps was obtained by a determination of the trinitrate intrinsic viscosity (a measure of the weight-average degree of polymerization). The degree of polymerization (D.P.), as such, was not used throughout the investigation since the available methods for the determination of the conversion constant K were not in agreement ($\underline{K} = (D.P.)/[\eta]_T$).

The eight pulps were then oxidized with lead tetraacetate at 50°C. using a concentration ratio of 1:1 (moles tetraacetate:moles anhydroglucose). From the oxidation curves (consumption of oxidant versus time), from an investigation of the oxidized pulp and oxidation solution, and from a general study of the oxidation, the following results were obtained:

1. A high correlation (correlation coefficient equals 0.981) was obtained between the mannose unit percentage of a pulp sample and the extrapolated value (a measure of the initial, rapid consumption) of lead tetraacetate consumption during the oxidation of that sample. This corroborates the work of Steinmann and White (1). For sulfite pulps only, the correlation coefficient equals 0.992;

2. A high correlation (correlation coefficient equals 0.978) was obtained between the xylose unit percentage of a pulp sample and the total tetraacetate consumption (after 600 minutes of oxidation). This, in part, corroborates the work of both Steinmann and White (1) and Roudier and Nick (20);

3. The correlation between the degree of polymerization of a pulp and its extent of oxidation is very slight;

4. The correlation between the sorption ratio of a pulp and its consumption of oxidant is low. The correlation, however, does not completely define the exact influence of accessibility--partly because of the limited number of pulps used in the study. Almost certainly, an interaction of variables occurs. For sulfite pulps only, the correlation coefficient equals 0.93.

5. Data was obtained increasing the knowledge of the effect of the temperature and concentration of reactants during the oxidation. The importance of the measurement of a "blank-decay" curve was established and a precise technique for the determination of the lead tetraacetate consumption was formulated.

6. Lowered pulp yields were found in the oxidized pulps and a concurrent indication of the presence of partly oxidized oligosaccharide fragments was made in the oxidation solution.

7. The tentative identification of an oxidation product, erythrose, was made in a limited hydrolyzate fraction obtained from the oxidized pulp.

8. After the oxidation (and subsequent "stopping" and washing operations) an analysis of the partly oxidized pulp showed the loss of approximately 60% of the mannose units originally present in the unoxidized pulps. A similar analysis showed the loss of approximately 30% of the original xylose units, again confirming the work of Roudier and Nick (20) who found that xylose is of less importance than mannose although quite significant. Approximately 10% of the original glucose units present in the unoxidized pulps was lost.

9. The extent of the mannose unit loss (45-72%) that was observed in this investigation was considerably greater than that observed by Roudier and Nick (20) (16-40%). The temperature of the oxidation (50°C., in contrast to 30°C., the temperature employed by Roudier and Nick) is believed to be an important factor in accounting for this difference.

10. It is believed that the concentration of oxidant to pulp that was used in the oxidation (approximately four times as large as that used by Roudier and Nick) contributed little to the extent of the differences in mannose units lost. Both Roudier and Nick, and this investigator, found the concentration variable to be of little importance in the oxidation.

CONCLUSIONS

The data and other information presented in this report warrant the following conclusions:

1. Mannose units are preferentially (partially) removed from a pulp during the lead tetraacetate oxidation process under the conditions of temperature and concentration employed during this study. This selective removal of mannose units is thus in agreement with the findings of Roudier and Nick (20).

2. The greatest removal of mannose units from an oxidized pulp occurs during the initial portion of the oxidation--say, the first 230 minutes of reaction.

3. A lesser removal of xylose units is found upon oxidation of a pulp. Again, this conclusion is in agreement with the findings of Roudier and Nick.

4. The degree of polymerization has a negligible influence upon the subsequent oxidation of a pulp.

5. The importance of the accessibility of a pulp, as such, in influencing the subsequent oxidation of that pulp with lead tetraacetate is secondary to the percentage of mannose in the pulp. As has been discussed throughout this report though, the exact influence of the accessibility has not been completely defined—partly because of the limited number of pulps used in this study.

6. The removal or "loss" of sugar units during an oxidation is not attributable to oxidation alone; rather, the "mechanism" of the removal is probably an oxidation followed by a limited hydrolysis or solution of those sugar units in, perhaps, the more accessible, amorphous portions of the oxidized pulp. The determination of a lowered yield in the oxidized pulp and the indication of oligosaccharide fragments in the oxidation solution, thus, in part, verify the aforementioned "mechanism" of the sugar removal.

7. That an oxidation of the 2,3-glycol grouping of a hexose unit occurs is indicated by the tentative identification of erythrose in a hydrolyzate of the partly oxidized pulp.

SUGGESTIONS FOR FUTURE WORK

Polglase (59) has stated that a continuation of Steinmann and White's investigation (1) might lead to a quantitative method for the determination of mannose units—at least for less refined pulps with a moderate mannose unit content. Roudier and Nick (20) have indicated such a method to be unfeasible due to the low oxidation of mannose units (16-40%) obtained with pulps, even during prolonged oxidation.

It is this author's opinion that there is a need for studying methods of increasing the oxidation. Changing the oxidation temperature from 30°C. to 50°C. resulted in an increased oxidation—and also an increased mannose unit removal (45-72%). The use of a catalyst to promote glycol fission by lead tetraacetate has been indicated by Bell, Rivlin, and Waters (60) and might be a method of increasing the oxidation.

It would be interesting to know how the glucomannans behave toward lead tetraacetate. The glucomannans are unique in that the mannose: glucose ratio is 3-4:1, the accessibility may be very great, and the degree of polymerization very low (61-65). An investigation would provide information about both the glucomannans, and the lead tetraacetate oxidation.

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APPENDIX I

VISCOSITY AND ACCESSIBILITY DETERMINATIONS

VISCOSITY

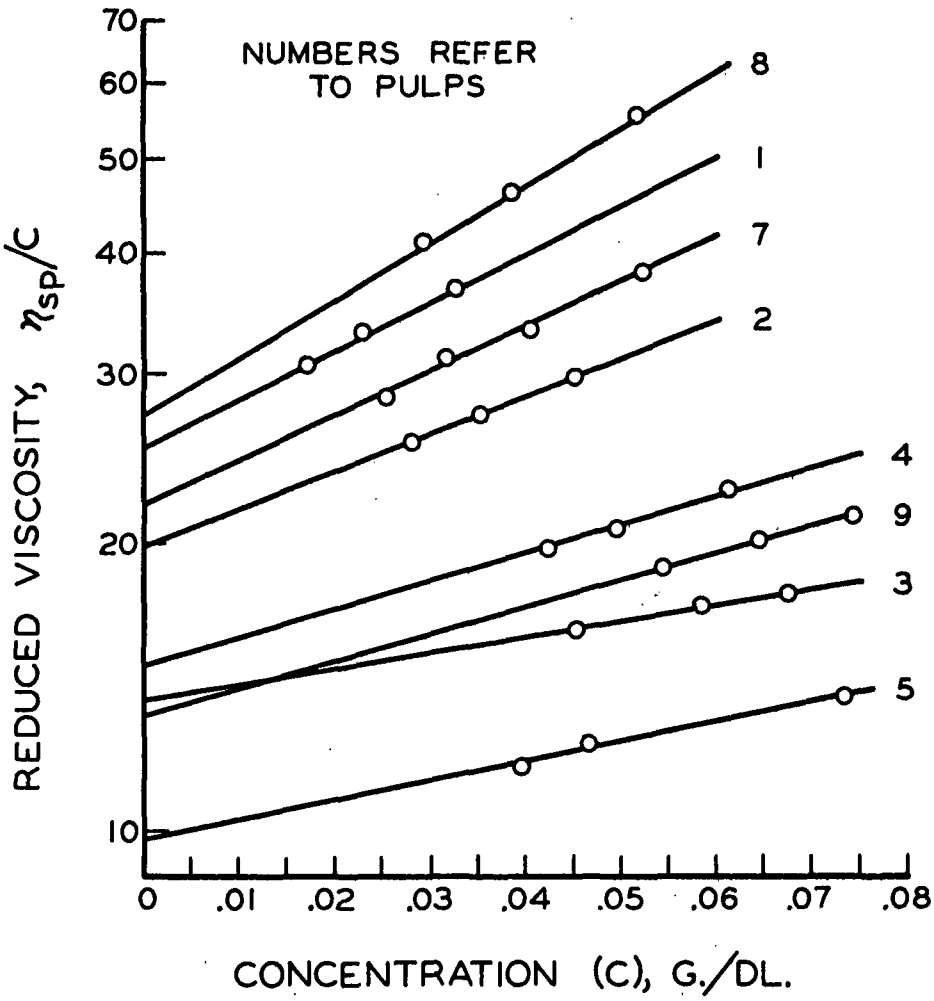

Figure 15. Determination of Intrinsic Viscosity[a]

[a] Intrinsic Viscosity $[\eta] = \lim_{C \to 0} \frac{\eta_{sp}}{c}$

where (37):

$$\log \frac{\eta_{sp}}{c} = \log [\eta] + K [\eta] c$$

TABLE XV

DETERMINATION OF TRINITRATE INTRINSIC VISCOSITIES

Pulp No.	Intrinsic Viscosity, $[\eta]$ dl./g.	Nitrogen, %	Average Nitrogen, %	Trinitrate Intrinsic Viscosity, $[\eta]_T$ dl./g.
1	25.3	13.80 13.41 13.67	13.63	29.9
2	19.7	14.22 14.10	14.15	19.7
3	13.7	14.01 14.04	14.03	14.2
4	14.8	14.07 14.12	14.10	15.0
5	9.8	14.08 13.92	14.00	10.3
7	21.9	13.98 14.03	14.01	22.9
8	27.2	13.99 13.88 13.94	13.94	29.1
9	13.2	13.86 13.92	13.89	14.3

ACCESSIBILITY

TABLE XVI

DETERMINATION OF SORPTION RATIO

Pulp No.	Moisture Regain, %[a]	Average Moisture Regain, %	Sorption Ratio[b]
1	5.48 5.35	5.42	1.00
2	6.26 6.06	6.16	1.14
3	7.12 7.17	7.15	1.32
4	6.27 6.54	6.41	1.18
5	6.23 6.25	6.24	1.15
7	7.58 7.29	7.44	1.37
8	7.32 7.33	7.33	1.35
1[c]	5.82 5.73	5.78	1.00
9[c]	6.62 6.81	6.72	1.16

[a] Pulps conditioned 114 hours, 73°F., and 50% relative humidity.

[b] Sorption ratio may be defined as the moisture regain of the pulp divided by the moisture regain of Pulp No. 1, cotton linters. Thus, the average moisture regain percentages of Pulp Nos. 2-8 were divided by 5.42, while the average moisture regain percentage of Pulp No. 9 was divided by 5.78.

[c] Determined several weeks later.

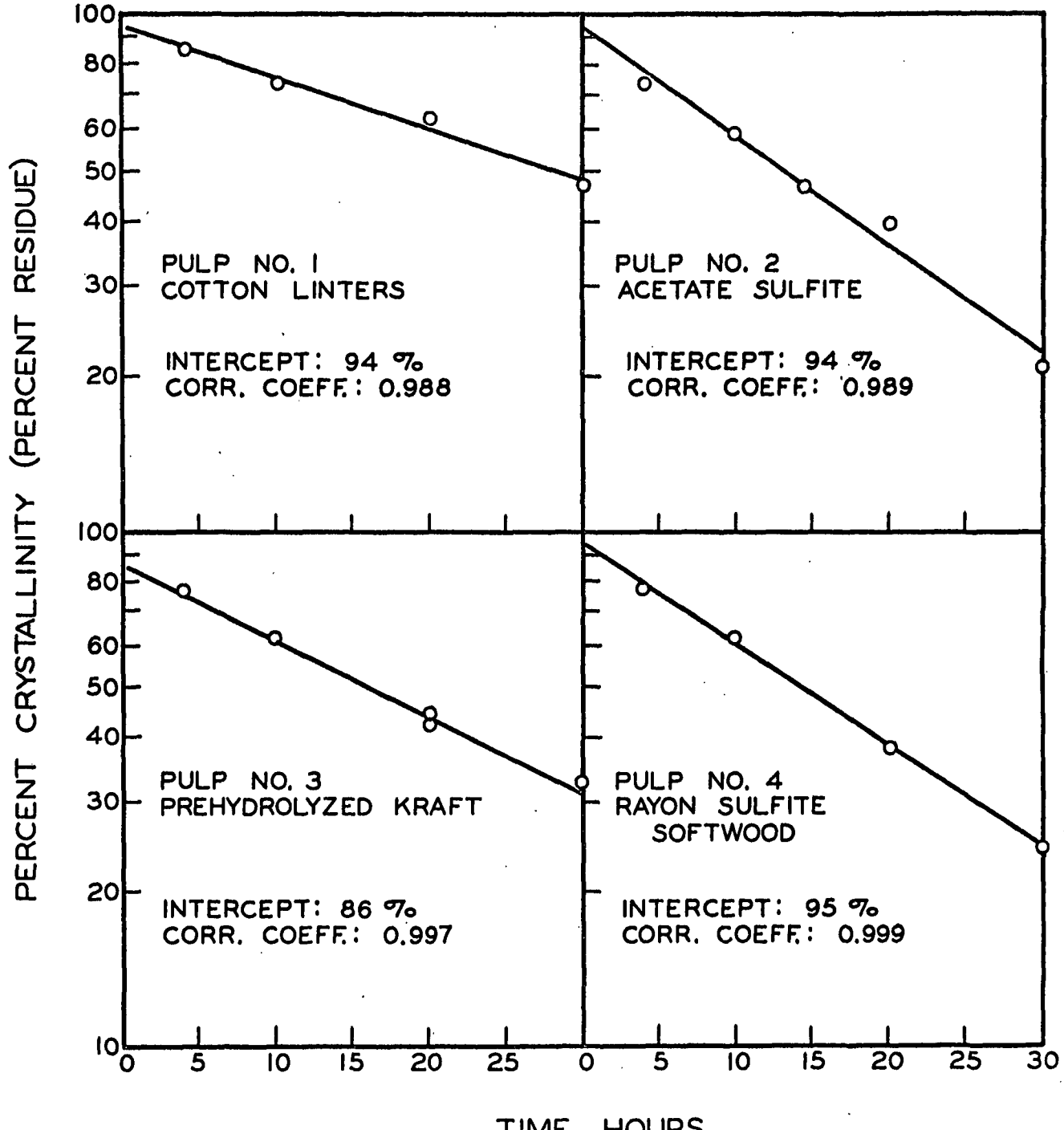

Figure 16a. Determination of Hydrolysis Crystallinities

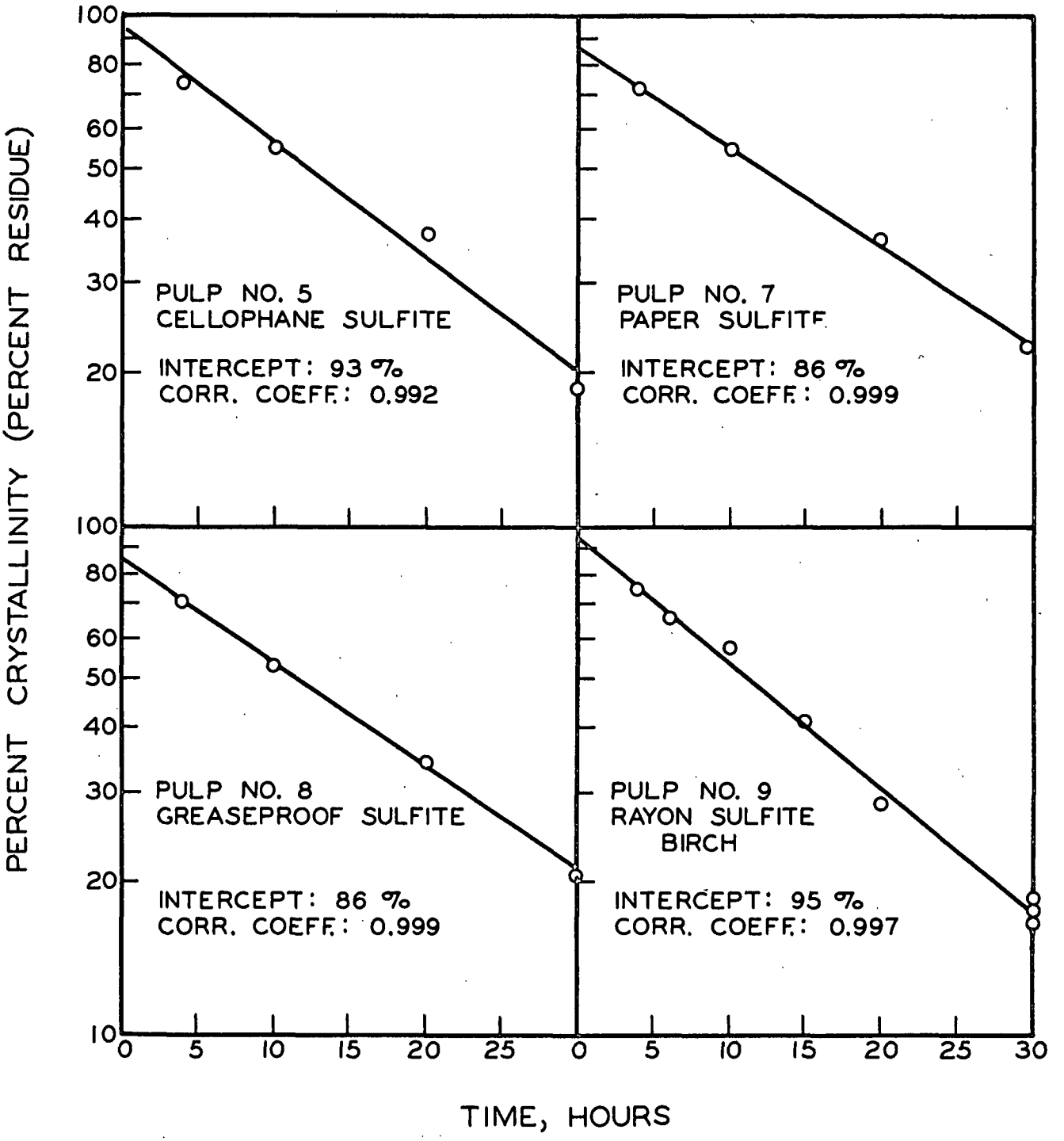

Figure 16b. Determination of Hydrolysis Crystallinities

Humic Acid Corrections of Hydrolysis Crystallinities

The weights of all residues were corrected for the formation of humic substances by the application of the equation developed by Philipp, Nelson, and Ziifle (28):

$$h = \frac{\left[\frac{f^2 g^2}{1/kt + fg}\right]}{2}$$

where

h = g. humic substances/50 ml. hydrochloric acid;

f = constant, independent of acid concentration, glucose concentration, or temperature, = 0.07;

g = initial glucose concentration, g./100 ml.;

k = rate constant, = 1.5 (4N HCl, 100°C.); and,

t = time of hydrolysis, hours.

APPENDIX II

SUGAR UNITS CONTENT DETERMINATION

PROCEDURE

Purification of o-Aminobiphenyl

The o-aminobiphenyl is purified by dissolving the impure reagent into a minimum quantity of absolute ethanol at 30-35°C. Charcoal and "Celite" are added and the mixture filtered through a Celite pad.

The filtrate is poured into a beaker, a few drops of water are added to "cloud" the filtrate, and the beaker is placed into an ice bath. The crystals that precipitate are filtered, washed with absolute ethanol (-15°C.), and placed in a desiccator to dry.

The filtrate and washings that remain are again combined with a few drops of water and cooled to -15°C. The crystals that form are washed with cold ethanol and dried in a desiccator.

Melting point (experimental): 48.5-49.5°C.

Melting point (literature): 49.0-50.0°C. (66).

Quantitative Analysis

The following procedure is a modification (67) of the chromatographic, spectrophotometric method, developed by Timell, Glaudemans, and Currie (47) and modified by Piper and Bernardin (48).

Pulps are subjected to a total hydrolysis by the method of Saeman and co-workers (45). Approximately 0.3 g. of fluffed pulp is weighed

into a vial. Three milliliters of 72% sulfuric acid are added and the vial is placed in a 30°C. bath for one hour. The sample is stirred as required to effect solution.

The contents are then transferred to a 250-ml. beaker containing 84 ml. water and autoclaved for one hour at a steam pressure of 15 ± 1 p.s.i. The solution is cooled and stirred with about 25 g. of freshly-washed Amberlite IR-45 carbonate form ion-exchange resin. The exact amount of resin should be such as to raise the pH to 3.8 in 20-30 minutes.

The neutralized hydrolyzate is then decanted through a filter. Quantitative washing is not necessary since the ratio of carbohydrate constituents will supply the desired information.

Individual chromatographic papers (Whatman No. 1) are washed with distilled water for two 24-hour periods in a chromatographic tank reserved for this purpose. It is important that the paper be thoroughly dried between washing stages.

No more than four samples are spotted on a sheet 7-1/2 inches wide. It is desirable that each sugar in the spot be in a concentration range of 20-100 micrograms. The washed papers should be spotted within one day of the final washing period.

The developer is ethyl acetate:acetic acid:water (9:2:2, v/v). Baker analyzed, reagent-grade 99.8% glacial acetic acid was found to be satisfactory. The spotted sheets are conditioned overnight in the vapor phase of the developer.

The sheets are developed at constant temperature (25°C.) in the dark. A development time of approximately 28 hours is required. When more developer is required (during the course of development) it should be added through small, rubber-stoppered holes in the tank lid. (The lid should not be removed.) The developed papers are dried in air for not longer than one day.

The spray reagent and eluent is prepared as follows: Weigh 0.8 g. purified o-aminobiphenyl into a 50-ml. beaker. Wash with Baker 99.9% glacial acetic acid into a 200-ml. volumetric flask. Add about 150 ml. acetic acid and 32 ml. water to the contents of the flask and dissolve the reagent. Make to volume with 99.9% acetic acid. The reagent is prepared no more than one hour before using.

The chromatograms are sprayed as uniformly as possible and then heated at 103-105°C. for exactly five minutes. The heating will bring out the sugar spots.

The sugar spots are outlined with pencil under long-wave ultraviolet light. The spots are cut from the paper, weighed, and cut into 18 x 150 mm. test tubes. Blanks, equal in weight to the largest and smallest spot, are cut from the sheet, weighed, and cut into test tubes.

Six milliliters of the spray reagent are pipetted into each test tube and also into an empty tube (for standardization of the spectrophotometer). The tubes are tightly stoppered, shaken for at least 25 minutes, and filtered through glass wool.

Test tubes containing the glucose and blank filtrates are heated for 45 minutes on a boiling water-bath, rubber stoppers covered with aluminum foil being inserted in each test tube after the first minute; test tubes containing mannose and xylose filtrates are heated 30 minutes.

The test tubes are cooled in a cold water bath. Optical densities are read on a Beckman DR quartz spectrophotometer at 380 millimicrons with a slit width of 0.08 mm.

STANDARD SOLUTIONS: CONVERSION FACTORS

The optical density of a solution, as measured in a spectrophotometer, may be multiplied by a "factor" to obtain the number of micrograms (gammas) of sugar in that solution. For a "known" or standard solution, the situation is reversed: by dividing the number of gammas of a sugar dissolved in a solution by its optical density, the conversion factor may be obtained. Since Beer's Law (optical density is proportional to concentration) holds, the conversion factor should remain constant provided the gammas dissolved in solution are within the limit of the law. The variation, then, in the "known" conversion factors provides the means for determining the precision of the analysis.

Standard solutions of glucose, mannose, and xylose were prepared by dissolving an exact weight of sugar in an exact volume. All optical densities were corrected for the "blank." Table XVII gives the "raw" conversion factors that were obtained. (The conversion factor equals gammas/corrected optical density.)

TABLE XVII

RAW CONVERSION FACTORS

Date of Analysis	Conversion Factor Glucose	Mannose	Xylose	Sum of Average Factors
1-22-59	255	275	269	
	248	278	259	
	253	---	258	
	254	---	---	
Average:	(253)	(277)	(262)	792
% of Total:	31.9	35.0	33.1	
1-29-59	244	277	245	
	239	257	---	
	236	267	---	
Average:	(240)	(267)	(245)	752
% of Total:	31.9	35.5	32.6	
2-5-59	219	237	---	
	216	245	---	
	223	---	---	
Average:	(219)	(241)	---	
2-12-59	223	258	222	
	219	265	217	
	---	266	220	
Average:	(221)	(263)	(220)	704
% of Total:	31.4	37.4	31.3	
2-19-59	214	244	227	
	223	248	220	
	---	241	221	
Average:	(219)	(244)	(223)	686
% of Total:	31.9	35.6	32.5	
Average factor for weeks of 2-5-59 & 2-19-59	219	243	223	
Average % (all weeks excluding 2-12-59)	31.9	35.4	32.7	

From Table XVII, two important points may be noticed: (1) the factors obtained for the first two weeks are higher than for the last three, although the corresponding percentage figures are "constant," and (2) the factors obtained for the week of 2-12-59 may be in error and should, perhaps, be disregarded.

It is believed that changes in the recently recrystallized o-aminobiphenyl accounted for variations in the conversion factor during the two weeks in January. After several weeks, the factors approached a constant value. It has been found also, by other investigators, that if the o-aminobiphenyl is allowed to "stabilize" for several weeks after recrystallization, this discrepancy is absent (67, 68).

The factors, then, were placed on a "common denominator" basis by correcting by the ratio of percentages and by the ratio of averages. For example, the mannose conversion factor 278 for the week of 1-22-59 was revised as follows:

$$\text{Revised Factor} = \frac{278}{277} \times \frac{35.0}{35.4} \times 243 = 241$$

The conversion factors may be revised since the ultimate sugar percentages are expressed on a ratio basis and not on an absolute basis. (One could use the percentage figures in Table XVII as conversion factors and obtain the same sugar unit percentages.)

In Table XVIII, the revised conversion factors for the two weeks of January are given. (The conversion factors for the other weeks are unchanged.)

In order to ascertain whether to accept or reject the values for the week of 2-12-59, a statistical "Student T Test" will be applied. Once the mean conversion factor ($\bar{x}_1$) for the week of 2-12-59 and the mean for all other values ($\bar{x}_2$) is calculated—and their respective variances ($S^2_{\bar{x}_1}$ and $S^2_{\bar{x}_2}$) obtained—a "t" value may be obtained from:

$$S_p^2 = \frac{(n_1 - 1)S_{\bar{x}_1}^2 + (n_2 - 1)S_{\bar{x}_2}^2}{n_1 + n_2 - 2},$$

$$t = \frac{|\bar{x}_1 - \bar{x}_2| - 0}{S_p\sqrt{\frac{1}{n_1} + \frac{1}{n_2}}};$$

where n_1 and n_2 are the number of values used in calculating $\bar{x}_1$ and $\bar{x}_2$.

TABLE XVIII

REVISED CONVERSION FACTORS

Date	Conversion Factor		
	Glucose	Mannose	Xylose
1-22-59	221	241	233
	215	239	224
	219	—	223
	220	—	—
1-29-59	223	253	223
	218	235	—
	215	244	—

At the 95% confidence level, a value of $t_{97.5}$ may be obtained from a statistical table (54) (using $n_1 + n_2 - 2$ degrees of freedom). If the values of $t_{97.5}$ exceed that of the calculated t, the values for the week of 2-12-59 must be accepted.

When these calculations are made, it is found that the conversion factors for glucose and xylose for the week of 2-12-59 must be accepted while those for mannose must be rejected; in other words, at the 95% confidence level, the conversion factors obtained for mannose during the week of 2-12-59 could not have come from the same population as those obtained other weeks.

In Table XIX the complete list of conversion factors that will be used to calculate the mean conversion factor for each sugar is given.

TABLE XIX

COMPLETE LIST OF REVISED CONVERSION FACTORS

	Conversion Factor		
	Glucose	Mannose	Xylose
	221	241	233
	215	239	224
	219	253	223
	220	235	223
	223	244	222
	218	239	217
	215	247	220
	219	244	227
	216	248	220
	223	241	221
	223	---	---
	219	---	---
	214	---	---
	223	---	---
$\bar{X}$	219.14	242.90	223.00

From Table XIX, the standard deviation and the coefficient of variation for each set of conversion factors may be calculated. In Table XX the results of these calculations are given.

TABLE XX

PRECISION OF THE CONVERSION FACTOR DETERMINATION

	Glucose	Mannose	Xylose
Mean conv. factor	219	243	223
95% Conf. limits	217-221	239-247	220-226
Std. deviation	3.3	5.1	4.4
Coeff. of var., %	1.48	2.09	1.99

For example (from Table XX), for glucose, it can be seen that other independent determinations of the conversion factor will produce a mean between 217 and 221, 95% of the time. In addition, the "percentage error" for this determination is approximately 1.48%.

Another independent investigator (68), working with glucose and xylose only, has obtained mean conversion factors for glucose and xylose of 219 and 223, respectively, thus in part confirming the results of Table XX.

AMOUNT OF SUGAR FOUND IN HYDROLYZED SAMPLES

By multiplying the corrected optical density for each sugar by its respective conversion factor, the equivalent micrograms (gammas) per "sugar spot" may be obtained.

In Table XXI, the various gammas of sugar found in the specified number of microliters (lambdas) are listed in duplicate. All values are uncorrected for variations in the rate of hydrolysis of glucose, mannose, and xylose. In order to convert the figures to a weight percentage, the average gammas in each duplicate pair should be divided by the following correction factors (45):

Glucose: 0.974
Mannose: 0.962
Xylose: 0.912

It may seem, after observing the figures in Table XXI that, in some cases, the glucose "pairs" are not good replications. It must be remembered that on a percentage basis, however, the figures are good duplicate pairs; i.e., nearly the same weight percentage figures will be

TABLE XXI

AMOUNT OF SUGARS FOUND IN HYDROLYZED SAMPLES

Pulp No.	Minutes Oxidized	Lambda Basis	Micrograms (Uncorrected) Glucose	Mannose	Xylose
1	0	10	93.7	0.0	0.42
			93.1	0.0	0.36
2	0	25	53.4	0.21	0.48
			53.5	0.20	0.63
3	0	25	57.3	0.57	0.57
			55.2	0.53	0.59
4	0	25	51.6	1.35	1.16
			53.5	1.38	1.08
4	600	7	69.5	0.74	1.28
			68.6	0.59	1.17
5	0	25	52.8	1.51	0.83
			53.9	1.26	0.63
5	600	4.3	58.7	0.53	0.66
			62.9	0.55	0.64
7	0	25	50.2	4.14	2.03
			46.5	4.07	2.63
7	230	7	84.8	3.00	2.65
			84.8	2.28	2.42
7	600	10	62.2	2.99	2.05
			61.1	3.05	2.25
8	0	20	33.3	4.55	1.91
			34.0	4.62	1.95
8 (repeat)	0	25	43.1	5.87	2.52
			42.5	5.53	2.36
8	65	8	61.3	5.15	2.41
			59.6	4.63	2.43
8	230	20	56.9	4.08	2.25
			53.4	4.00	2.60
8	625	20	55.2	3.30	2.40
			59.8	3.24	2.54
9	0	20	43.9	0.78	1.89
			43.7	0.62	---
9 (repeat)	0	25	49.6	0.58	1.77
			49.4	0.53	1.92
9	600	10	82.1	0.33	2.43
			79.9	0.25	2.34

obtained for the three sugars regardless of whether the high, low, or average glucose value is used since this value constitutes a very large percentage of the total amount in the specified volume of lambdas.

For example, from Table XXI, using the duplicate values for Pulp No. 8 (oxidized 625 minutes), the following calculations may be made:

Sugar	Gammas Uncorrected		Correction Factor		Gammas Corrected	Sugar Percentage
First Determination						
Glucose	55.2	/	.974	=	56.67	90.3
Mannose	3.30	/	.962	=	3.43	5.5
Xylose	2.40	/	.912	=	2.63	4.2
Second Determination						
Glucose	59.8	/	.974	=	61.40	90.9
Mannose	3.24	/	.962	=	3.37	5.0
Xylose	2.54	/	.912	=	2.79	4.1

Thus, it is seen that the difference in percentage figures will not alter the conclusions that have been formulated.

APPENDIX III

THE OXIDATION

PROCEDURE

At least two weeks prior to the oxidation, prepare a .02N thiosulfate solution (standardized by weight or by volume and specific gravity) and a lead tetraacetate "stock" solution containing approximately 28 g. lead tetraacetate per liter of Baker Reagent 99.8% glacial acetic acid.

Accurately weigh .27-g. quantities of pulp samples (dried four hours in a 107°C. oven), transfer to 500-ml. flasks (each containing a magnetic stirring bar), and place in a 50°C. water bath. The water bath should rest on the magnetic stirring motors.

Five milliliters of the lead tetraacetate stock solution are titrated with .02N sodium thiosulfate—the iodine being liberated by the addition of 50 ml. "stopping solution" (10 g. potassium iodide and 50 g. sodium acetate per 100 ml. water)—and the number of milliliters of stock tetraacetate and acetic acid needed to give 1.05 moles lead tetraacetate/mole anhydroglucose unit calculated. (The amounts used correspond to .001667 moles anhydroglucose.) Since a "blank oxidation" must also be prepared, solution for the blank must also be prepared. (Typical calculations are given in this section.)

Add 50 ml. portions of 99.8% acetic acid (of known weight) to the samples and blank flasks in the water bath, stopper, and, with stirring, allow two hours of activation. During the activation period, place stoppered flasks containing 110 ml. of the prepared lead tetraacetate solution in an auxiliary 50°C. water bath. (Have weights of flasks and solution recorded.)

After the two-hour activation, transfer the heated, prepared oxidizing solutions to the 500-ml. flasks (determine tares later) and immediately remove a 25-ml. aliquot from the blank, charge into a previously tared 125-ml. Erlenmeyer flask; weigh, add 55 ml. stopping solution, and titrate with .02N sodium thiosulfate dispensed from a weight-buret.

At other previously selected intervals, remove 25-ml. aliquots from the blank and sample flasks and repeat the above procedure. After removing an aliquot from a sample flask, add 290 ml. stopping solution to the pulp plus solution remaining in the flask; filter and wash the oxidized pulp with water, then with ethanol, and store in ethanol.

SAMPLE CALCULATIONS

Typical calculations are recorded below:

Normality of thiosulfate = .02053N

5 ml. tetraacetate "stock" solution ≡ 29.45 ml. thiosulfate

Then, to get ratio of 1.05/1 (mole/mole):

$$\left[\frac{1.05}{\frac{(.02053)}{(1000)(2)(.001667)}}\right] \times \frac{(5)}{(29.45)} = 28.95;$$

where, .001667 = moles anhydroglucose (.27 g. pulp).

Therefore, 28.95 ml. tetraacetate stock solution + 81.05 ml. acetic acid = 110 ml., the desired mixture.

If five sample flasks and one blank flask are to be prepared, multiplying the above figures by 6.16903 gives: 178.59 ml. lead tetraacetate stock solution and 500 ml. acetic acid.

By taking say, five blank aliquots during the oxidation, a decay curve for the blank may be obtained, and by subtracting the value for the sample from the corresponding point on the blank curve, and correcting for differences in aliquot weights, the Δg. (blank-sample) .02N thiosulfate per 26-g. aliquot may be obtained.

The calculations below are typical:

Specific gravity of .02053N thiosulfate at standardization temperature = 1.000065

Δg. .02053N thiosulfate/26 g. aliquot = 0.27 g.

Wt. 110 ml. lead tetraacetate solution + 50 ml. acetic acid = 167.01 g.

O.D. pulp sample weight = .2749 g. = .001697 moles

$$\left[\frac{(0.27)(167.01)}{(26.000)}\right] \times \left[\frac{(.02053)}{(1000)(2)(1.000065)(.001697)}\right]$$

$$= 1.049 \times 10^{-2} \text{ moles lead tetraacetate consumed per mole anhydroglucose unit (162 g. pulp).}$$

TABLE XXII

SUMMARY OF OXIDATION DATA[a]

Pulp No.	Time of Oxidation, min.	Oxidant Consumed[b]	Time of Oxidation, min.	Oxidant Consumed[b]
1	65	0.306	360	0.573
	150	0.307	455	0.574
	230	0.345	600	0.538
2	65	0.572	425	0.945
	140	0.870	460	1.132
	230	0.943	525	1.298
	360	0.937	600	1.367
3	65	0.0	300	0.461
	65	0.0	325	0.465
	140	0.546	450	0.813
	230	0.386	600	0.888
4	65	0.776	375	1.861
	140	1.273	460	2.215
	230	1.664	525	2.218
	360	1.590	600	2.512
5	40	0.708	305	1.488
	65	1.049	360	1.609
	110	1.087	425	1.704
	140	1.095	525	1.897
	200	0.966	600	1.952
	230	1.357		
7	65	1.486	375	3.579
	140	2.396	460	3.865
	230	3.095	460	3.707
	300	3.323	525	4.395
	360	3.591	600	4.520
8	65	2.077	360	4.405
	140	3.143	460	4.751
	230	3.694	525	5.004
	230	4.019	626	5.220
9	65	0.463	360	2.228
	125	1.503	460	2.588
	200	1.585	550	2.869
	230	1.739	600	3.234
	300	1.890		

[a] Figures 4a, 4b, and 4c present the data graphically.

[b] Moles lead tetraacetate x 10^2 consumed per mole anhydroglucose unit (162 g. pulp).

APPENDIX IV

ANALYSIS OF THE OXIDATION

CONSUMPTION OF LEAD TETRAACETATE

As was discussed in another section (see page 32) values of the lead tetraacetate consumption, other than the extrapolated, initial value, may be obtained by taking measurements from the oxidation curves (Figure 4a, 4b, and 4c) at any selected time of oxidation. Table XXIII lists some of these values.

TABLE XXIII

SELECTED CONSUMPTION VALUES OF LEAD TETRAACETATE

Pulp No.	Moles Lead Tetraacetate x 10^2 Consumed Per Mole Anhydroglucose Unit			
	Extrapolated (0 min.)	150 min.	350 min.	600 min.
1	0.26	0.36	0.47	0.59
2	0.76	0.88	1.06	1.27
3	0.27	0.40	0.60	0.83
4	1.08	1.35	1.90	2.48
5	0.85	1.15	1.55	2.03
7	2.14	2.51	3.50	4.50
8	3.07	3.26	4.35	5.23
9	0.76	1.33	1.97	3.18

CORRELATIONS

When values of lead tetraacetate consumption, other than the extrapolated, initial values, are plotted against selected independent variables, a variety of correlation coefficients are observed. In Table XXIV, these coefficients are listed.

TABLE XXIV

CORRELATION COEFFICIENTS

Independent Variables	Dependent Variables: Consumption of Lead Tetraacetate — Extrapolated (0 min.)	150 min.	350 min.	600 min.
Mannose, %	0.981	0.961	0.952	0.901
Xylose, %	0.866	0.924	0.944	0.978
Mannose + Xylose, %	0.980	0.984	0.984	0.958
Insoluble in 18% NaOH, %	0.922	0.961	0.967	0.969

SAMPLE CALCULATIONS: SUGAR REMOVAL AFTER OXIDATION

Using Pulp No. 8 and the average yield percentage value (88.0%) as an example, and using the "sugar percentage data" of Table XIIb (see page 47), calculations of the following type may be made:

Basis: 100 grams of unoxidized pulp

Original sugar percentage (and weight) of unoxidized pulp:

Glucose: 83.5 g. (%)
Mannose: 11.4 g. (%)
Xylose: 5.1 g. (%)

After oxidation, 88.0 g. remaining (average 88.0% yield).

Using the final sugar percentages of the oxidized pulp:

Glucose: (90.6%)(88) = 79.7 g.
Mannose: (5.2%)(88) = 4.6 g.
Xylose: (4.2%)(88) = 3.7 g.

Therefore, the percentage sugars based upon 100 g. unoxidized pulp are:

Glucose: 79.7%
Mannose: 4.6%
Xylose: 3.7%

And, in order to compute the percentage sugar lost:

[(83.5 - 79.7)/(83.5)] x 100 = 4.6% glucose lost.

[(11.4 - 4.6)/(11.4)] x 100 = 59.6% mannose lost.

[(5.1 - 3.7)/(5.1)] x 100 = 27.5% xylose lost.

To compute grams of sugar lost per 100 grams of unoxidized pulp:

83.5 - 79.7 = 3.8 g. glucose lost.

11.4 - 4.6 = 6.8 g. mannose lost.

5.1 - 3.7 = 1.4 g. xylose lost.